Asian Journal of Chemistry; Vol. 23, No. 7 (2011), 2874-2878

ASIAN JOURNAL OF CHEMISTRY

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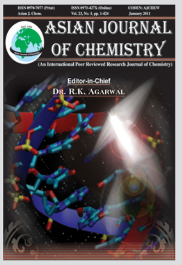

Photocatalytic Degradation of Methyl Orange by Ni^{2+}-Doped Anatase $TiO_2/CoFe_2O_4$ Composites Under Solar Light Irradiation

FANG DENG[1,2], YUEXIANG LI[1,*], SHAOQIN PENG[1], XUBIAO LUO[2,*] and SHENGLIAN LUO[2]

[1]School of Science, Nanchang University, Nanchang 330031, P.R. China
[2]School of Environmental and Chemical Engineering, Nanchang Hangkong University, Nanchang 330063, P.R. China

*Corresponding authors: E-mail: liyx@ncu.edu.cn (Y. Li); luoxubiao@126.com (X. Luo)

(*Received*: 8 July 2010; *Accepted*: 4 March 2011) AJC-9690

Ni^{2+}-doped anatase $TiO_2/CoFe_2O_4$ (Ni^{2+}-$TiO_2/CoFe_2O_4$) composites with core-shell structure were prepared by an ultrasonic method. The core $CoFe_2O_4$ nanoparticles were synthesized *via* co-precipitation method and the photoactive shell Ni^{2+}-doped TiO_2 nanoparticles were directly coated on the $CoFe_2O_4$ by the ultrasonic-induced hydrolysis reaction of tetrabutyl titanate in a nickel(II) sulfate aqueous solution, then the composites were calcined at different temperature. The resultant Ni^{2+}-$TiO_2/CoFe_2O_4$ composites exhibited good magnetic response. The photocatalytic activities of Ni^{2+}-$TiO_2/CoFe_2O_4$ composites were evaluated by the photocatalytic degradation of methyl orange under solar light irradiation. The results showed that Ni-doping concentration and calcined temperature had effect on the photocatalytic activities of Ni^{2+}-$TiO_2/CoFe_2O_4$ composites. Ni^{2+} doping effectively improved photocatalytic activities of $TiO_2/CoFe_2O_4$ composites and the photocatalytic activities of Ni^{2+}-$TiO_2/CoFe_2O_4$ with an optimal doping concentration of 1.5 % were four times that of undoped $TiO_2/CoFe_2O_4$. Moreover, H_2O_2 assisted Ni^{2+}-$TiO_2/CoFe_2O_4$ composites under solar light irradiation was an effective and promising process for decolourization of dye-containing wastewater.

Key Words: Ni^{2+}-doped anatase $TiO_2/CoFe_2O_4$, Ultrasonic-induced, Methyl orange, Photocatalytic degradation, Solar light irradiation.

INTRODUCTION

Photocatalysis has been continuously developed as a promising alternative technology for environmental purification[1-3]. Generally, titania (TiO_2) is the most promising semiconductor photocatalyst for environmental purification, due to its good characteristics of powerful oxidation strength, chemical stability, nontoxicity and inexpensiveness. However, separation and recovery of the nano-sized photocatalysts are intrinsic and significant obstacles for practical application because of its small particle size[4,5].

In order to solve the problem of separation and recovery, many efforts have been made in the immobilization of photocatalysts on the substrates, such as glass, quartz and stainless steel[6-8]. However, the photocatalytic activity of titania-coated system declines greatly due to the fact that the effective surface area of the photocatalysts and mass-transfer rate decreases after immobilization[9].

Generally, a photocatalytic reaction conducted in a suspension of the photocatalysts offers the best degradation effect. Research has been carried out by immobilizing catalyst onto a magnetic core nanoparticles, such as Fe_3O_4/ZnO[10] and Fe_3O_4/CdS[11] for the purpose of simple separation and good dispersibility. The magnetic photocatalysts could be easily separated and recovered from the suspension by applying an appropriate magnetic field. However, the problem faced by photocatalysis of magnetic photocatalysts was the unfavourable electronic interaction between the nonmagnetic material and magnetic core, which would lead to an increase in the photogenerated electron/hole recombination and a decrease of photocatalytic activity[12-17]. To improve their photocatalytic properties, the inert layer including silica[18], carbon[19] and polymers[20] was coated on the surface of magnetic materials before immobilizing catalyst. The inert layer can reduce the adverse effect, but lead to the reduction of magnetic responsivity.

In order to improve the photocatalytic activity of magnetic TiO_2 without the reduction of magnetic response, the shell Ni^{2+}-doped TiO_2 nanoparticles were directly coated on the $CoFe_2O_4$ by the ultrasonic-induced hydrolysis reaction of tetrabutyl titanate in a nickel(II) sulfate aqueous solution. Subsequently, the photocatalytic activities of the composites on the degradation of methyl orange were investigated in detail.

EXPERIMENTAL

Cobalt chloride hexahydrate, ferric chloride hexahydrate, sodium hydroxide, methyl orange and hydrogen peroxide

(30 %) were of analytical grade and were used without further purification. Poly(ethylene glycol) 6000 (PEG6000) and were chemical reagent grade. Water was purified through a Milli-Q water system (Bedford, USA).

Preparation of Ni^{2+}-doped anatase $TiO_2/CoFe_2O_4$ (Ni^{2+}-$TiO_2/CoFe_2O_4$) composites

Preparation of $CoFe_2O_4$ nanoparticles: $CoFe_2O_4$ was prepared by adding 10 mL of NaOH (6 mol L^{-1}) to 10 mL of an acid solution of $FeCl_3$ (0.4 mol L^{-1}) and $CoCl_2$ (0.2 mol L^{-1}) at 80 ºC and under vigorous stirring and stirring was continued for another 1 h at this temperature to allow the growth of nanoparticles. After the solution was cooled down to room temperature, the precipitate was isolated by a magnetic field and washed with distilled water until neutral.

Pretreatment of $CoFe_2O_4$ nanoparticles by PEG: $CoFe_2O_4$ nanoparticles were dispersed in 20 mL of 2 % PEG solution by ultrasonic treatment for 0.5 h and subsequent vigorous stirring for 1 h. The suspension was allowed to stand for more than 6 h and then the aqueous solution of PEG was decanted, leaving only PEG adsorbed on $CoFe_2O_4$ nanoparticles to obtain the modified $CoFe_2O_4$ (PEG-$CoFe_2O_4$).

Preparation of Ni^{2+}-$TiO_2/CoFe_2O_4$ composites: The PEG-$CoFe_2O_4$ was dispersed into 40 mL $NiSO_4$ aqueous solution (the atomic ratios of Ni to Ti = 0, 0.5, 1.0, 1.5, 2.0, 2.5 nominal atomic % (at. %)) in an ultrasonic bath for 0.5 h, then the solution were adjusted to pH 5 with dilute sulfuric acid. Tetrabutyl titanate ($Ti(OC_4H_9)_4$, TBOT) was used as a titanium source. Tetrabutyl titanate (32.5 mL) was added dropwise to the above solution for 45 min at thermostatic bath about 20 ºC. The ultrasonic system is 2 s on and 2 s off in air during the whole reaction. After ultrasonic reaction, the wet gel was dried under vacuum at 80 ºC for about 10 h. The obtained white xerogel was calcined at 500 ºC in air for 3 h. To further investigate the effect of calcined temperature on the photocatalytic activity of the as-prepared catalysts, the sample (Ni:Ti = 1.5 at. %) was also calcined at 300, 400, 500 and 600 ºC in air for 3 h, respectively.

Photocatalytic degradation of methyl orange: The photolysis of methyl orange was carried out in an Erlenmeyer flask under sun irradiation on the roof of Nanchang Hangkong university from 10 am to 3 pm, using 100 mL, 20 mg/L the dye solution and 2 g/L Ni^{2+}-$TiO_2/CoFe_2O_4$ composites. The degradation was followed by Schomazou UV/Visible spectrophotometer. The intensity of solar radiation (1050 W m^{-2}) was measured by using solar meter. It fluctuates during the reaction even under clear sky. However, we kept the solar experiments of required reaction under identical conditions, by carrying out the experiments simultaneously, side by side, thus making it possible to compare results of photodegradation.

According to the transformation of absorbance before and after illumination, the degradation rate of methyl orange can be calculated as follows: $D = (A_0 - A)/A_0$, where D is degradation rate, A_0 is the absorbance of initial methyl orange and A is the absorbance after illumination.

Characterization of Ni^{2+}-$TiO_2/CoFe_2O_4$ composites: The crystal structure of the catalysts was characterized by X-ray diffraction (XRD) analysis which was taken on a D8 advance diffractometer (Bruker Company) using CuK_α radiation.

Magnetic characteristics of Ni^{2+}-$TiO_2/CoFe_2O_4$ composites were measured by using LDJ-9600 vibrating sample magnetometer (VSM, America LDJ Company).

RESULTS AND DISCUSSION

XRD analysis: The crystal structure of titania greatly affects photocatalytic activity. Therefore, the phase characterization of Ni^{2+}-$TiO_2/CoFe_2O_4$ composites was investigated by XRD. XRD patterns of the prepared Ni^{2+}-$TiO_2/CoFe_2O_4$ composites with Ni/Ti atomic ratio of 1.5 at. % calcined at 500 ºC are shown in Fig. 1. The two expected phases ($CoFe_2O_4$ and TiO_2 anatase) were identified in the pattern. The XRD pattern shows crystalline structure of the pure anatase phase. The dominant peaks at 2θ about 25.3º, 37.9º, 48.0º, 53.9º, 55.1º, 62.7º and 75.3º represent the indices of (101), (004), (200), (105), (211), (204) and (215) plane of anatase TiO_2, respectively. The corresponding main diffraction peaks of magnetic $CoFe_2O_4$ appear. The occurrence of the dominant peaks at 2θ about 30.0º, 35.4º, 43.0º, 56.9º and 62.5º, which correspond to the indices of (220), (311), (400), (511) and (440), respectively, indicates the presence of the $CoFe_2O_4$ in the Ni-doped anatase TiO_2. Moreover, the presence of rutile TiO_2 phase was not detected, showing that the method led to the production of pure anatase.

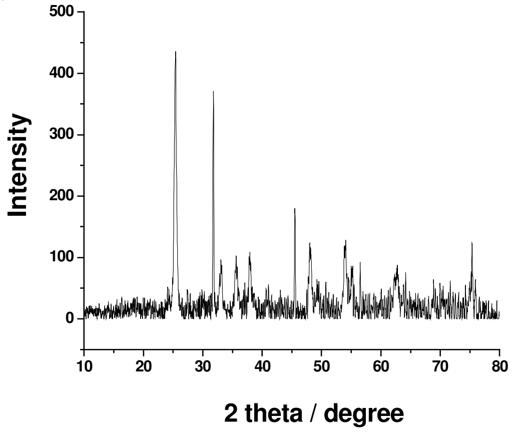

Fig. 1. XRD patterns of Ni^{2+}-$TiO_2/CoFe_2O_4$ composites prepared at a Ni/Ti atomic ratio of 1.5 at. % and calcined at 500 ºC

It is interesting to note that nickel oxide or Ni_xTiO_y phases are not found in the patterns of XRD, which is in accord with the results reported by Jing *et al.*[21] (no diffraction peaks assigned to crystalline of nickel species could be detected). There are two reasons responsible for this. One probable reason is that the concentration of Ni-doping is so low that it can not be detected by XRD. The other is that Ni^{2+} has an ionic radius similar to Ti^{4+} and can also form octahedral coordination as Ti^{4+} does and all the nickel ions may be insert into the structure of titanium and locate at interstices or occupy some of the titanium lattice sites, forming an iron-titanium oxide solid solution[21,22].

In general, the full width at half maximum of XRD peak is related to the particle size of crystal materials. The larger the width, the smaller the size crystallites have. The mean crystallite size can be calculated from full-width at half-maxima of XRD peak by using Debye-Scherrer formula:

$$D_{\text{Scherrer}} = \frac{k\lambda}{\beta\cos\theta}$$

where λ is the wavelength of the X-ray radiation ($\lambda = 0.154056$ nm), K is the Scherrer constant (K = 0.89), θ is the characteristic X-ray radiation ($\theta = 12.65°$) and β is the full-width-at-half-maximum of the (101) plane (in radians)[23]. Based on the XRD results, it is estimated that the average crystal size is 16.2 nm.

Magnetic responsibility of Ni^{2+}-$TiO_2/CoFe_2O_4$ composites: Fig. 2 shows the plots of magnetization *versus* magnetic field (M-H loop) at 25 °C for Ni^{2+}-$TiO_2/CoFe_2O_4$ composites. It is apparent that there is no hysteresis and both remanence and coercivity are zero, suggesting that the Ni^{2+}-$TiO_2/CoFe_2O_4$ composites were superparamagnetic. Superparamagetism of Ni^{2+}-$TiO_2/CoFe_2O_4$ composites illustrates that Ni^{2+}-$TiO_2/CoFe_2O_4$ composites respond magnetically to an external magnetic field and this response vanishes upon the removal of the field. The saturation magnetization of Ni^{2+}-$TiO_2/CoFe_2O_4$ composites is 77.74 emu/g, indicating that the Ni^{2+}-$TiO_2/CoFe_2O_4$ composites could be easily and quickly separated from a sample solution within a short time through placing a strong magnet or an applied magnetic field.

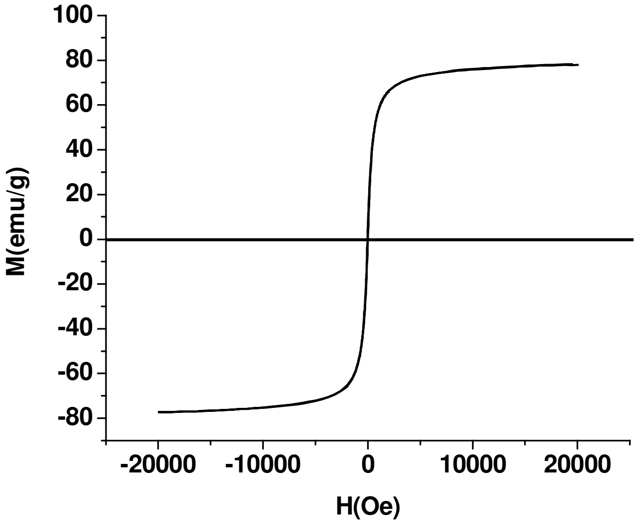

Fig. 2. Magnetization curve of Ni^{2+}-$TiO_2/CoFe_2O_4$ composites prepared at a Ni/Ti atomic ratio of 1.5 at. % and calcined at 500 °C

Photocatalytic degradation of methyl orange by Ni^{2+}-$TiO_2/CoFe_2O_4$ composites:

Effect of calcined temperature on photocatalytic degradation of methyl orange: Many studies have shown that calcination is an effective treatment method to enhance the photoactivity and crystallization of nanosized TiO_2 photocatalysts[24,25]. Fig. 3 shows the effect of calcined temperature on photodegradation activity of the Ni^{2+}-$TiO_2/CoFe_2O_4$ composites with an optimal doping concentration of 1.5 %. With increasing calcination temperature, the photocatalytic activity of the Ni^{2+}-$TiO_2/CoFe_2O_4$ increases due to the decrease of the surface defects in the Ni^{2+}-$TiO_2/CoFe_2O_4$ composites and enhancement of crystallization. At 500 °C, the Ni^{2+}-$TiO_2/CoFe_2O_4$ composites display highest photocatalytic activity. With further increasing calcined temperature to 600 °C, the photodegradation activity decreases rapidly. Therefore, the highest photocatalytic activities of the Ni^{2+}-$TiO_2/CoFe_2O_4$ composites calcined at 500 °C can be ascribed to synergetic effects of good crystallization, appropriate phase composition and slower recombination rate of photogenerated charge carriers.

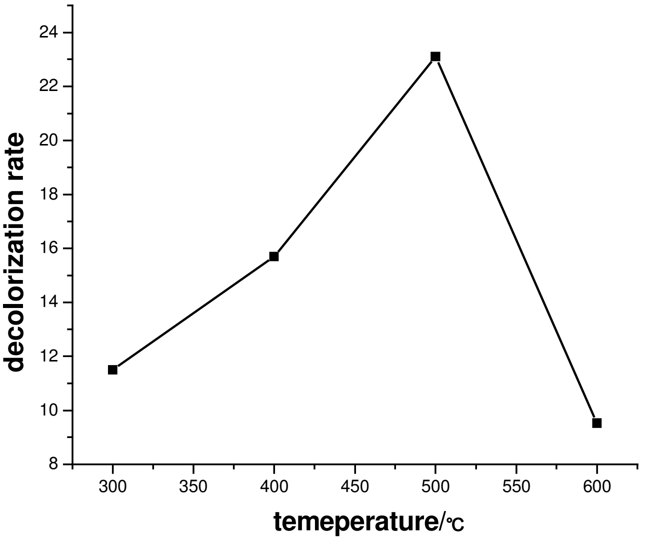

Fig. 3. Effect of calcination temperature on the photocatalytic degradation activity of Ni^{2+}-$TiO_2/CoFe_2O_4$ (Ni/Ti = 1.5 at. %)

Effect of Ni-doping concentration on photocatalytic degradation of methyl orange: Fig. 4 shows the effect of Ni^{2+}-doping concentration on photodegradation activity of the Ni^{2+}-$TiO_2/CoFe_2O_4$ composites calcined at 500 °C. It is observed that, upon increasing Ni^{2+} concentration, the decolourization rate initially increases, goes through a maximum for photocatalysts containing 1.5 % Ni^{2+} and then decreases obviously for higher dopant concentrations.

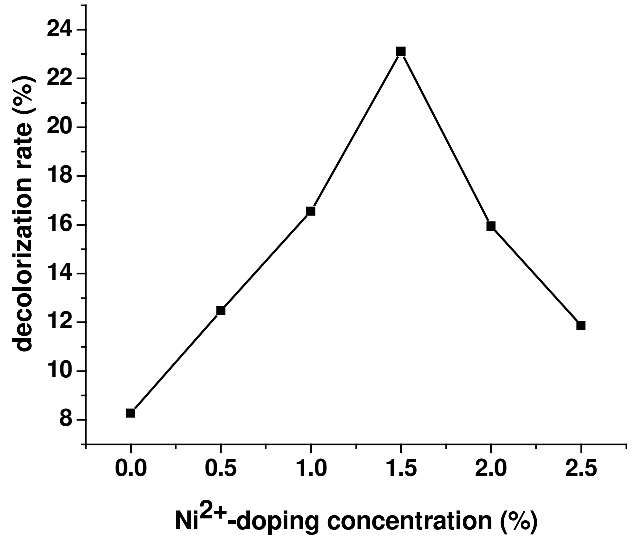

Fig. 4. Effect of Ni-doping concentration on the photocatalytic degradation activity of Ni^{2+}-$TiO_2/CoFe_2O_4$ calcined at 500 °C

The effect of Ni^{2+}-doping concentration on the photocatalytic activity of Ni^{2+}-$TiO_2/CoFe_2O_4$ under solar light irradiation should be due to the reason that an appropriate amount of Ni^{2+} can induce more photo-generated electrons and holes to participate in the photocatalytic reactions. Apart from this effect, an appropriate amount of Ni^{2+} ions can act as intermediates for photo-generated holes and electrons transfer and inhibit the recombination of holes and electrons[26]. At higher Ni^{2+}-doping concentration, Ni^{2+} ions act as recombination centers which reduce the photocatalytic activity of the material[27]. The possible surface reactions are as follows:

$$\mathrm{Ni^{2+} + e^- \rightarrow Ni^+}$$

$$\mathrm{Ni^{2+} + h^+ \rightarrow Ni^{3+}}$$

$$\mathrm{Ni^{3+} + OH^- \rightarrow Ni^{2+} + OH}$$

$$\mathrm{Ni^+ + O_2 \rightarrow Ni^{2+} + O_2^-}$$

Effect of irradiation time on photocatalytic degradation of methyl orange: The comparison of photocatalytic degradation rate with undoped and Ni^{2+}-doped $TiO_2/CoFe_2O_4$ composites under solar light irradiation at different moments is shown in Fig. 5. Degradation rate of methyl orange by Ni^{2+}-doped $TiO_2/CoFe_2O_4$ and undoped $TiO_2/CoFe_2O_4$ increases rapidly at the beginning and then adsorption rate decreases in later stage until reaching adsorption equilibrium within 210 min. However, the photocatalytic activity of Ni^{2+}-$TiO_2/CoFe_2O_4$ composites with an optimal doping concentration of 1.5 % is much higher than that of undoped $TiO_2/CoFe_2O_4$.

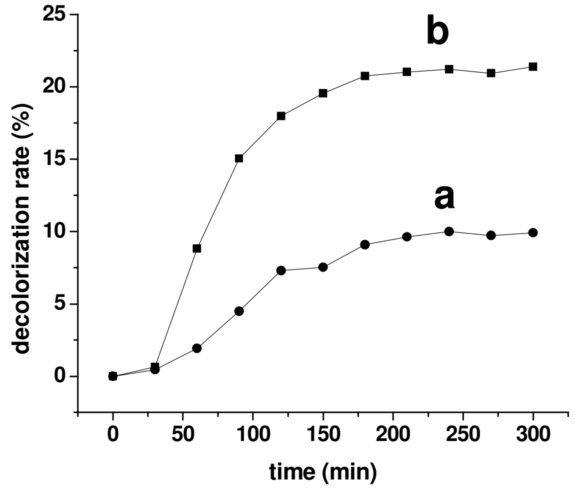

Fig. 5. Photodegradation of MO by (a) undoped $TiO_2/CoFe_2O_4$ and (b) Ni^{2+}-$TiO_2/CoFe_2O_4$ (Ni/Ti = 1.5 at. %) catalysts as a function of solar light irradiation time

Effect of H_2O_2 on photocatalytic degradation of methyl orange: In photocatalytic reaction of semiconductors, the major energy-wasting step is the electron-hole recombination which leads to inactivity or low quantum yield. Hence, the prevention of electron-hole recombination becomes very important. This can be achieved by adding proper electron acceptor such as H_2O_2 to the system[28].

H_2O_2 has been found to enhance the degradation rate of compounds due to more efficient generation of hydroxyl radical ($OH^{\bullet}$) and inhibition of electron/hole (e^-/h^+) pairs recombination by trapping the conduction band electron and generating more radicals and other oxidizing species according to the following equations[29]:

$$\mathrm{H_2O_2 + O_2^{'} \rightarrow OH + OH^- + O_2}$$

$$\mathrm{H_2O_2 + h\nu \rightarrow 2OH^{\bullet}}$$

$$\mathrm{H_2O_2 + e_{CB}^- \rightarrow OH^{\bullet} + OH^-}$$

Hydroxyl radical ($OH^{\bullet}$) is a super strong oxidant and dominant species in photocatalytic process and able to oxidize a variety of organic substances completely on the surface of catalyst under light irradiation[30]. As a result, proper addition of H_2O_2 facilitated the generation of hydroxyl radicals and promoted the photodecolourization effectively.

Fig. 6 shows the effect of H_2O_2 on photocatalytic activity of the Ni^{2+}-$TiO_2/CoFe_2O_4$ composites in view of photocatalytic degradation of methyl orange under solar light irradiation. The results show that degradation rate of methyl orange reaches 83.56 % in the presence of H_2O_2. The combination of H_2O_2 and solar light irradiation has proved to enhance degradation rates when compared to solar light irradiation in the absence of H_2O_2.

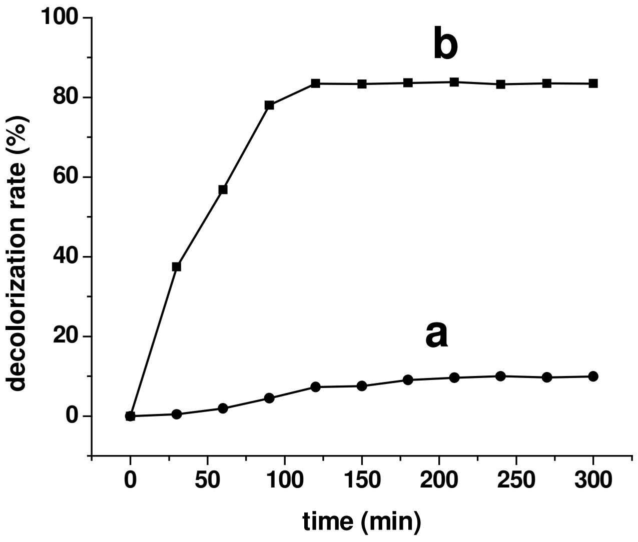

Fig. 6. Effect of H_2O_2 addition on the photocatalytic degradation activity of Ni^{2+}-$TiO_2/CoFe_2O_4$ (Ni/Ti = 1.5 at. %) calcined at 500 ºC. (a) in absence of H_2O_2, (b) the concentration of H_2O_2 is 0.326 mol/L

Conclusion

Ni^{2+}-doped anatase $TiO_2/CoFe_2O_4$ composites with core-shell structure were prepared by an ultrasonic method. The core, $CoFe_2O_4$ nanoparticles were synthesized *via* co-precipitation method and the shell Ni^{2+}-doped TiO_2 nanoparticles were directly coated on the $CoFe_2O_4$ by the ultrasonic-induced hydrolysis reaction of tetrabutyl titanate in a nickel(II) sulfate aqueous solution, then followed by heat-treating at different temperature. The photocatalytic activity of the prepared Ni^{2+}-$TiO_2/CoFe_2O_4$ composites was measured by the photodegradation of methyl orange under solar light irradiation and results indicated that Ni-doping concentration and calcined temperature had great effect on photocatalytic activities of the Ni^{2+}-$TiO_2/CoFe_2O_4$ composites. Moreover, the photocatalytic activity of Ni^{2+}-$TiO_2/CoFe_2O_4$ composites was enhanced after addition of H_2O_2.

ACKNOWLEDGEMENTS

This work was financially supported by China National Funds for Distinguished Young Scientists (No. 50725825), The National Basic Research Program of China (973 Program) (No. 2005CB623901) and Natural Science Foundation of China (No. 50978132).

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