

## ZnFe<sub>2</sub>O<sub>4</sub> nanoparticle: Synthesis and photocatalytic activity under UV-Vis and visible light

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### Abstract

In the present work, the ZnFe<sub>2</sub>O<sub>4</sub> nanoparticle has been successfully synthesized. The obtained sample was characterized by X-ray diffraction (XRD) and emission scanning electron microscopy (FE-SEM) and its optical property were examined by UV-Vis spectrophotometer. FE-SEM revealed that the particle size of the ZnFe<sub>2</sub>O<sub>4</sub> of about 47 nm was synthesized. The photocatalytic performance under UV-Vis and visible light was evaluated by decolorization of congo red (CR) anionic dye solution. The UV-Vis and visible light irradiation source consist of a high pressure mercury lamp 400 W and filament tungsten lamp 100 W respectively. The photocatalytic results show that the ZnFe<sub>2</sub>O<sub>4</sub> sample can degrade (CR) dye solution up to 100% after 30 and 120 min under UV-Vis and visible irradiation respectively.

**Keywords:** ZnFe<sub>2</sub>O<sub>4</sub>; photocatalyst; visible light; congo red.

### Introduction

Magnetically separable photocatalysts have been widely applied in the treatment of dye pollutants in wastewater [1-5]. Spinel ferrite with a general formula of MFe<sub>2</sub>O<sub>4</sub> is a magnetic material. Many methods such as refluxing [6] hydrothermal [7-9], thermal decomposition [10], mechanochemical [11] and microwave-hydrothermal assisted ionic liquid [12] have been reported for the synthesis of zinc ferrite. Obviously, fabrication of zinc ferrite *via* a simple approach and, further, exploring its novel properties continue to be a challenge. The photocatalytic reaction, based on UV-Vis irradiated semiconductor provides electrons in the conduction band and holes in the valence band. These charge carriers can recombine, or the holes can be scavenged by oxidizing species and electron by reducible species in the solution, finally, led to the destruction of many organic substances to CO<sub>2</sub>, H<sub>2</sub>O and corresponding mineral acids [13-17]. Organic dyes have

been extensively used for textile application. During textile manufacturing processes, a large quantity of wastewater containing dyestuffs is introduced into the aquatic system. It is necessary to find an effective, visible light driven photocatalyst for wastewater treatment. Until now, efforts have been made to develop efficient visible light and magnetically separable photocatalyst [18-22]. Various spinel ferrites have been used for degradation of contaminants [23-25]. Many researchers have been reported zinc ferrite alone or as composites efficiently degrade dye pollutants [26-29]. In this work, new synthesis for the ZnFe<sub>2</sub>O<sub>4</sub> nanoparticle was presented and the ability of ZnFe<sub>2</sub>O<sub>4</sub> to degrade congo red dye solution under UV-Vis and Visible light was examined.

### Experimental

#### Materials

Fe(NO<sub>3</sub>)<sub>3</sub>, 9H<sub>2</sub>O, Zn(NO<sub>3</sub>)<sub>2</sub>. 6H<sub>2</sub>O, NaOH and cethyl trimethyl ammonium bromide

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(CTAB) were used to prepare the zinc ferrite sample. All the analytical chemicals were purchased from Merck.

#### *Synthesis procedure for preparing ZnFe<sub>2</sub>O<sub>4</sub>*

In this procedure, 6 mmol of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, 3 mmol of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 40 mmol of NaOH, 0.548 mmol of (CTAB) and 15 mL distilled water were used. Above, chemical materials were stirred vigorously using magnetic stirrer for 2 hours at room temperature; the product was washed with double distilled water several times and dried at room temperature. Then, the product was annealed at 500 °C for 1 h.

#### *Evaluation of photocatalytic activity*

A High pressure mercury lamp 400 W manufactured by Philips, Holland, and filament tungsten lamp 100W manufactured by Pars Shahab, Iran, were used as the UV-Vis and visible light source, respectively. In the mercury lamp, the light produced is lines 404.7, 453.8, 546.1 and 577.6 nm, plus ultra-violet (UV) energy and to the filament tungsten lamp it is (500-700) nm in the visible region. The dye solutions of congo red 5 and 20 ppm were prepared as an environmental pollutant model. Air was blown into the dye solutions by an aquarium pump to maintain the solution saturated by oxygen. In each photocatalytic experiment, the amount of the prepared catalyst 0.5 g/l was used. During irradiation, agitation was maintained by a magnetic stirrer to keep the suspension homogeneous. The suspension was sampled at regular intervals and immediately centrifuged to completely remove catalyst particles. Then, the degree of photo decolorization (X), as a function of time, is given by  $X = (C_0 - C)/C_0$  where  $C_0$  is the initial concentration of dye, and C the concentration of dye at time t. The disappearance of peak at  $\lambda = 498$  nm was chosen for monitoring dye decolorization for congo red.

#### **Results and discussion**

The morphology and structure of the sample were characterized by using field

emission scanning electron microscope (FE-SEM), Hitachi S-4160 with gold coating and XRD (Holland Philips Xpert, X-ray diffractometer with Cu-K $\alpha$  radiation) respectively. Figure 1 shows that the morphology of the ZnFe<sub>2</sub>O<sub>4</sub> sample is nanoparticle and particle size is of about 47 nm.

The crystallite size and phase characteristic of the product were determined by using the XRD pattern. The XRD result (Figure 2) shows that the ZnFe<sub>2</sub>O<sub>4</sub> with cubic phase was obtained (JCPDS No. 82-1049). The crystallite size (D) of the ZnFe<sub>2</sub>O<sub>4</sub> sample was estimated using Scherrer's equation as follows [7, 30]:

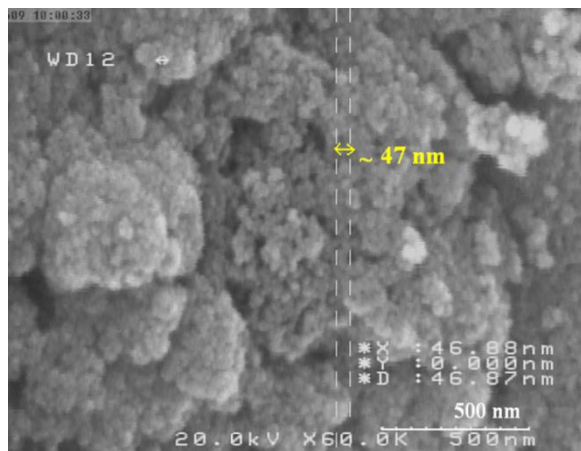
$$D = \frac{(0.9)\lambda}{\beta \cos\theta} \quad \text{Eq. (1)}$$

where  $\lambda$ ,  $\theta$ , and  $\beta$  are the X-ray wavelength (0.154056 nm for Cu-K $\alpha$ ), Bragg diffraction angle, and the full width at half maximum of the diffraction peak (FWHM), respectively. In this calculation, we took the highest intensity peak (311). According to Eq (1), the crystallite size of the synthesized ZnFe<sub>2</sub>O<sub>4</sub> was calculated about 17.7 nm. Figure 3a illustrates UV-Vis spectra of the ZnFe<sub>2</sub>O<sub>4</sub> sample. To have a quantitative estimate of the sample optical band gap, the Tauc Equation was employed (Eq. 2) [7, 31, 32].

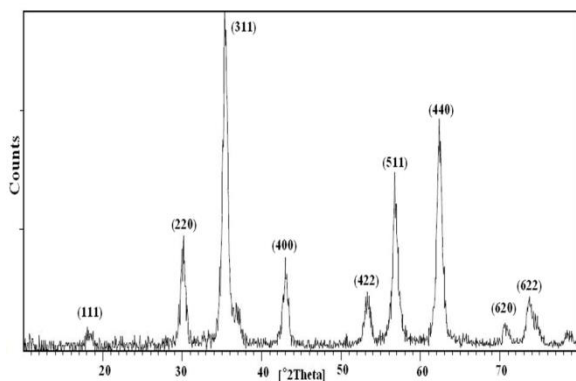
$$\alpha h\nu = A(h\nu - E_g)^\gamma \quad \text{Eq. (2)}$$

where  $\alpha$  is the absorption coefficient,  $h\nu$  is the photon energy,  $E_g$  is the optical band gap, A is a constant which does not depend on the photon energy and  $\gamma$  has four numeric values ( $\frac{1}{2}$  for the allowed direct transitions, 2 for the allowed indirect, 3 for the forbidden direct and  $\frac{3}{2}$  for the forbidden indirect optical transitions). In this work, the direct transition band gap ( $E_g$ ) of the sample was determined by plotting  $(\alpha h\nu)^2$  versus  $h\nu$  curve with the extrapolation of the linear region to  $(\alpha h\nu)^2 = 0$ . Figure 3b shows that the value of band gap for the synthesized ZnFe<sub>2</sub>O<sub>4</sub> is found to be 2.3 eV. Until now, band gap energy of zinc ferrite

was reported about 2.0, 1.9, 1.7 and 1.6 eV. by many researchers [33-35].



**Figure 1.** FE-SEM image of the ZnFe<sub>2</sub>O<sub>4</sub> sample



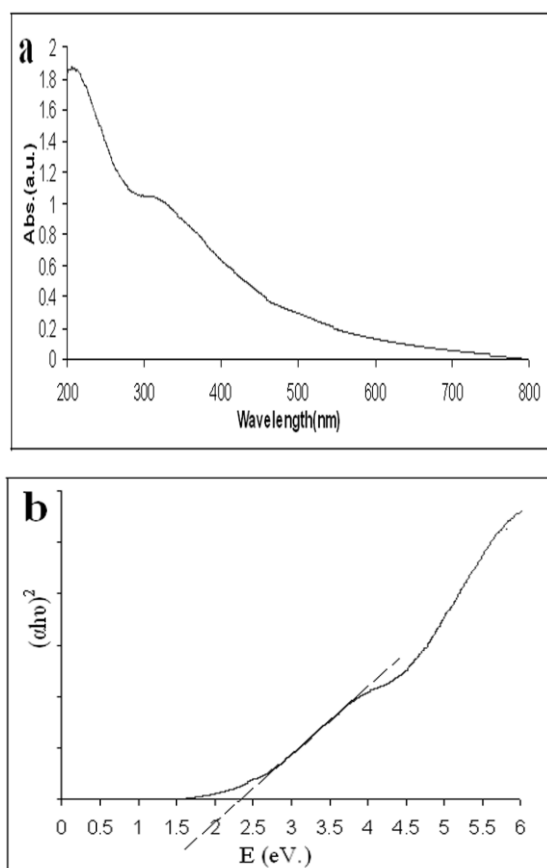
**Figure 2.** XRD pattern of the ZnFe<sub>2</sub>O<sub>4</sub> sample

The photocatalytic activity of the prepared sample was evaluated by the decolorization of the CR solution under the UV-Vis and visible irradiation. Figure 4a and 4b show that the ZnFe<sub>2</sub>O<sub>4</sub> sample can degrade congo red dye solution (5ppm) after 30 and 120 min under UV-Vis and visible irradiation respectively. Controlled experiment was performed by exposing a CR solution to the light source without the presence of the ZnFe<sub>2</sub>O<sub>4</sub>. Results show that the CR solution cannot be photo degraded in the absence of the ZnFe<sub>2</sub>O<sub>4</sub> under UV-Vis and visible light irradiation. Therefore, it is important to know how much CR dye solution is adsorbed on the ZnFe<sub>2</sub>O<sub>4</sub> catalyst surface. Hence, the adsorption degree of CR on the surface of the sample was measured in the dark. The adsorption experiment indicates that 64% of CR dye

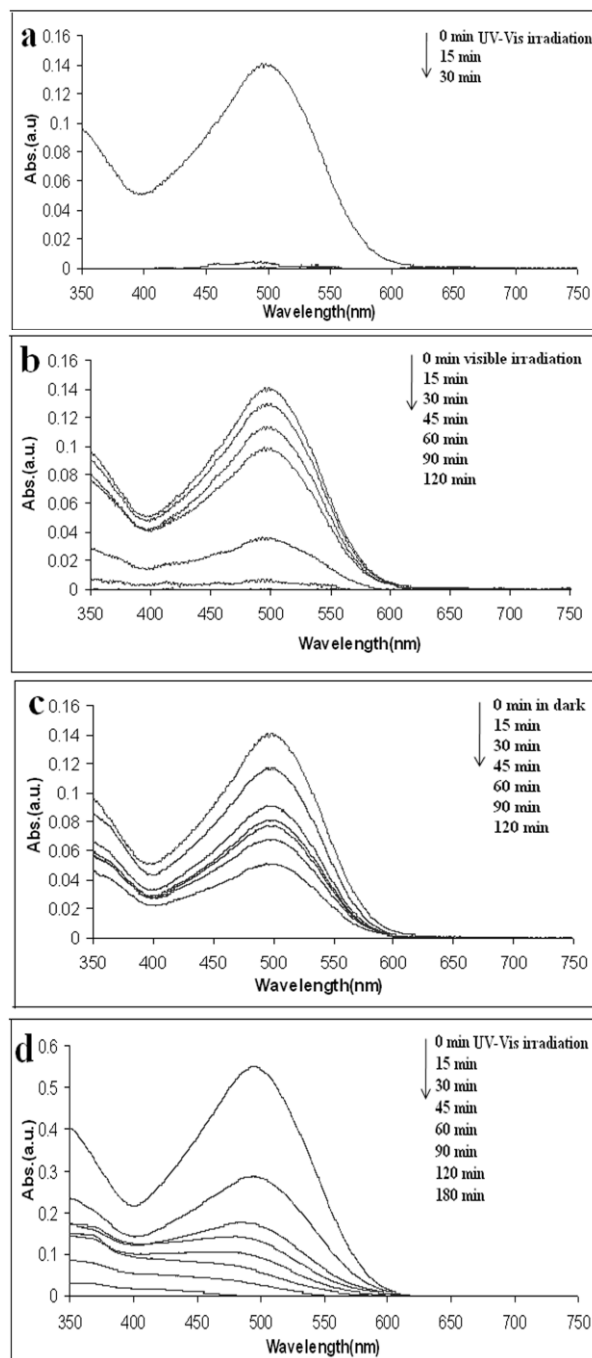
solution (5ppm) was adsorbed on the surface of the ZnFe<sub>2</sub>O<sub>4</sub> sample after 120 min (Figure 4c). The amount of (CR) adsorbed on the surface of the catalyst at the time *t* was calculated *via* the following equation [36]:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad \text{Eq. (3)}$$

where,  $q_t$  (mgg<sup>-1</sup>) is the adsorbed dye amount on the surface of the catalyst,  $C_0$  and  $C_t$  (mgL<sup>-1</sup>) are dye concentration at the initial and any time *t*, respectively. *V* is the solution volume (L), and *m* is the adsorbent mass (g). The maximum adsorption capacity of CR on the surface of the ZnFe<sub>2</sub>O<sub>4</sub> was obtained about 6.5 mgg<sup>-1</sup> after 120 min at 25 °C (Figure 5). The comparison of these experiments shows that the ZnFe<sub>2</sub>O<sub>4</sub> has good photocatalytic performance under UV-Vis and visible illumination. For further research, the photocatalytic experiment for decolorization of CR solution with 20 ppm concentration was carried out. The result indicates that ZnFe<sub>2</sub>O<sub>4</sub> sample can degrade CR solution (20 ppm) up to 98% during 180 min under UV-Vis irradiation (Figure 4d). Until now, the photocatalytic activity of Zinc ferrite was investigated by many researchers summarized in table 1. As can be seen in table 1, the prepared ZnFe<sub>2</sub>O<sub>4</sub>, in this work, has good photocatalytic activities for decolorization of the congo red dye solution under UV-Vis and visible light.



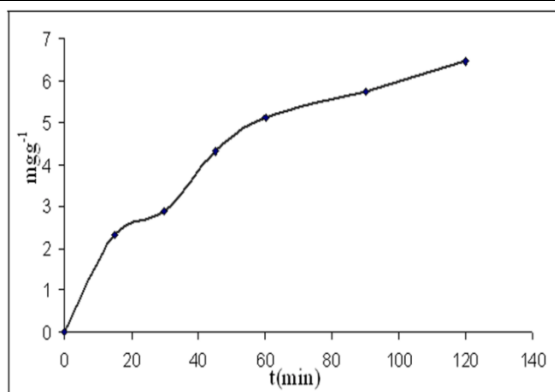
**Figure 3.** UV-Vis spectra of the  $ZnFe_2O_4$  sample (a), plot of the  $(ah\nu)^2$  versus  $h\nu$  (b)



**Figure 4.** UV-Vis spectra changes of congo red dye solution in presence of the  $ZnFe_2O_4$  sample (a) 5 ppm concentration of (CR) dye, UV-Vis irradiation (b), 5 ppm concentration of (CR) dye, visible irradiation (c), 5 ppm concentration of (CR) dye, in dark (d) and 20 ppm concentration of (CR) dye, UV-Vis irradiation

**Table 1.** Photocatalytic activity of ZnFe<sub>2</sub>O<sub>4</sub> for decolorization of various dye solutions in different condition recently published

Name of dye	Dye (mg/l)	Catalyst (mg/l)	Irradiation Source	Irradiation time (min)	Decolorization of dye (%)	Ref.
Rodamin B	20	0.8	Xe lamp (500 W)	300	100	[33]
Methyl Orange	10	0.4	$\lambda < 500$	60	75	[37]
Rodamin B	10	0.75	Xe lamp (300 W)	120	97.5	[34]
Rodamin B	20	0.5	Two 36 W H-type lamps	360	97	[35]
Methylene blue	5	1	Sunlight irradiation	360	85	[38]
Congo red	5	0.5	High presser Hg- lamp 400 W	30	100	In this work
Congo red	5	0.5	Filament tungsten lamp 100W	120	100	In this work
Congo red	20	0.5	High presser Hg- lamp 400 W	180	98	In this work



**Figure 5.** Adsorption capacity of (CR) dye on the surface of ZnFe<sub>2</sub>O<sub>4</sub>, T=25 °C

### Conclusion

In the present work, the ZnFe<sub>2</sub>O<sub>4</sub> nanoparticle has been synthesized using the simple procedure. Results indicate that the prepared ZnFe<sub>2</sub>O<sub>4</sub> has high photocatalytic activity under UV-Vis irradiation provided by a high pressure mercury lamp, 400 W and good photocatalytic activity under visible light irradiation provided by the filament tungsten lamp 100 W.

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### References

- [1] Z. Zhang, W. Wang, *Mater. Lett.*, **2014**, *133*, 212-215.
- [2] Y. Ao, J. Xu, D. Fu, X. Shen, C. Yuan, *Separation and Purification Tech.*, **2008**, *61*, 436-441.
- [3] A.A. Aziz, Y.H. Yan, G.L. Puma, C. Fischer, S. Ibrahim, S. Pichiah, *Chem. Eng. J.*, **2014**, *235*, 264-274.
- [4] J. Liu, D. Zhang, X. Pu, D. Dong, P. Cai, H.J. Seo, *Mater. Lett.*, **2014**, *130*, 94-97.
- [5] M. Shahid, L. Jingling, Z. Ali, I. Shakir, M.F. Warsi, R. Parveen, M. Nadeem, *Mater. Chem. Phys.*, **2013**, *139*, 566-571.
- [6] X. Cao, L. Gu, X. Lan, C. Zhao, D. Yao, W. Sheng, *Mater. Chem. Phys.*, **2007**, *106*, 175-180.
- [7] L. Han, X. Zhou, L. Wan, Y. Deng, S. Zhan, *J. Environ. Chem.*, **2014**, *2*, 123-130.

- [8] Z.P. Chen, W.Q. Fang, B. Zhang, H.G. Yang, *J. Alloys. Compd.*, **2013**, 550, 348-352.
- [9] Y. Koseoglu, A. Baykal, M.S. Toprak, F. Gozuak, A.C. Basaran, B. Aktas, *J. Alloys. Compd.*, **2008**, 462, 209-213.
- [10] F. Liu, X. Li, Q. Zhao, Y. Hou, X. Quan, G. Chen, *Acta Materialia.*, **2009**, 57, 2684-2690.
- [11] Z.Z. Lazarevic, C. Jovalekic, V.N. Lvanoveski, A. Recnik, A. Milutinouic, B. Cekic, N.Z. Romcevic, *J. Phys. Chem.*, **2014**, 75, 869-877.
- [12] S.W. Cao, Y.J. Zhu, C.F. Cheng, Y.H. Huang, *J. Hazard. Mater.*, **2009**, 171, 431-435.
- [13] S.Y. Lee, S.J. Park, *J. Indus. Eng. Chem.*, **2013**, 19, 1761-1769.
- [14] T. Ochiai, A. Fujishima, *J. Photochem. Photobiol. C.*, **2012**, 13, 247-262.
- [15] G.L. Puma, A. Bono, D. Kishnaiah, J.G. Collin, *J. Hazard. Mater.*, **2008**, 157, 209-219.
- [16] M. Sabbaghan, A.A. Firooz, V.J. Ahmadi, *J. Molecular Liquids.*, **2012**, 175, 135-140.
- [17] R.A. Mirzaie, F. Kamrani, A.A. Firooz, A.A. Khodadadi, *Mater. Chem. Phys.*, **2012**, 133, 311-316.
- [18] J.F. Guo, B. Ma, A. Yin, K. Fan, W.L. Dai, *Appl. Catal. B: Environ.*, **2011**, 101, 580-586.
- [19] J. Liu, S. Zuo, L. Yu, B. Li, P. Chen, *Particuology.*, **2013**, 11, 728-731.
- [20] X. Bian, K. Hong, L. Liu, M. Xu, *Appl. Sur. Sci.*, **2013**, 280, 349-353.
- [21] J. Cui, T. He, X. Zhang, *Catal. Commun.*, **2013**, 40, 66-70.
- [22] X. Li, C. Niu, D. Huang, X. Wang, X. Zhang, G. Zeng, Q. Niu, *Appl. Surf. Sci.*, **2013**, 286, 40-46.
- [23] T. Peng, X. Zhang, H. Lv, L. Zan, *Catal. Commun.*, **2012**, 28, 116-119.
- [24] H.S. Kim, D. Kim, B.B. Kwak, G.B. Han, M.H. Um, M. Kang, *Chem. Eng. J.* **2014**, 243, 272-279.
- [25] Z. Zhu, Q. Zhao, X. Li, Y. Li, C. Sun, G. Zhang, Y. Cao, *Chem. Eng. J.*, **2012**, 203, 43-51.
- [26] Y. Sun, W. Wang, L. Zhang, S. Sun, E. Gao, *Mater. Lett.*, **2013**, 98, 124-127.
- [27] S.W. Cao, Y.J. Zhu, G.F. Cheng, *J. Hazard. Mater.*, **2009**, 171, 431-435.
- [28] R. Shao, L. Sun, L. Tang, Z. Chen, *Chem, Eng. J.*, **2013**, 217, 185-191.
- [29] X. Li, D. Tang, F. Tang, Y. Zhu, C. He, M. Liu, C. Lin, Y. Liu, *Mater. Research. Bull.*, **2014**, 56, 125-133.
- [30] P.K. Harold, E.A. Leroy, X-ray Diffraction Procedure for Polycrystalline and Amorphous Materials, Wiley, New York, 1974.
- [31] S. J. Pearton, D. J. Norton, K. Ip, Y.W. Heo, T. Steiner, *Prog. Mater.Sci.*, **2005**, 50, 293-340.
- [32] S.C. Lyu, Y. Zhang, H. Ruh, H.J. Lee, H.W. Shim, E.K. Suh, C.J. Lee, *Chem. Phys. Lett.*, **2002**, 363, 134-138.
- [33] X. Li, Y. Hou, Q. Zhao, L. Wang, *J. Colloid inter. Sci.*, **2011**, 358, 102-108.
- [34] L. Han, X. Zhou, L. Wan, Y. Deng, S. Zhan, *J. Environ. Chem. Eng.*, **2014**, 2, 123-130.
- [35] C. Fan, Z. Gu, L. Yang, F. Li, *Chem. Eng. J.*, **2009**, 155, 534-541.
- [36] V. Belessi, G. Romanos, N. Boukos, D. Lambropoulou, C. Trapalis, *J. Hazard. Mater.*, **2009**, 170, 836-844.
- [37] S.D. Jadhav, P.P. Hankare, R.P. Patil, R. Sasikala, *Mater. Lett.*, **2011**, 65, 371-373.
- [38] Z. Jia, D. Ren, Y. Liang, R. Zhu, *Mater. Lett.*, **2011**, 65, 3116-3119.

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