

Enhanced stability and photocatalytic performance of transition metal-doped ZnO with magnetite nanoparticle and zeolite

M I Pratiwi^{1,2}, N Afifah^{1,2} and R Saleh^{1,2}

¹Department of Physics, Faculty of Mathematics and Natural Sciences Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia

²Integrated Laboratory of Energy and Environment, Faculty of Mathematics and Natural Sciences Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia

Corresponding author's e-mail: rosari.saleh@gmail.com

Abstract. The combination of zeolite and transition metal-doped ZnO nanoparticles for improved electron and hole photogeneration and inhibited electron-hole recombination, due to the trapping states, has been studied in our previous work. However, the photocatalyst has not been separated and reused after successfully degrading the organic dye. Therefore, in this study, we incorporated four different variations of magnetite nanoparticles into zeolite-supported Fe-doped ZnO, using the co-precipitation method. The samples were characterized with the aid of various measurements, such as x-ray diffraction, infrared absorption, diffuse reflectance spectroscopy, vibrating sample magnetometer (VSM), and Burneur-Emment-Teller (BET). The photocatalytic activity of nanocomposites was examined by photodegradation of methylene blue under UV light irradiation. The results show that the presence of a certain amount of magnetite nanoparticles in a zeolite-supported Fe-doped ZnO nanocomposite improved its efficiency in degrading methylene blue. The role of charged carriers and the active radical involved in the photocatalytic activity is discussed.

Keywords: ZnO, photocatalytic, natural zeolite, Fe-doped

1. Introduction

Photocatalysis is a process of organic pollutant degradation using light irradiation and a catalyst, which has attracted researchers' attention over the past few years [1-4]. Research into the issue has reached a high level of development, because it could be deployed to manage the water pollution issue wrought by the dye wastes produced by various chemical factories. In the photocatalytic process, the catalyst that could be used to degrade organic pollutant in water is a semiconductor. This is a promising approach, since it could degrade the organic pollutant without causing secondary pollution [1-2].

One of semiconductor that is commonly used as a photocatalytic is ZnO, mainly because its low-cost and band gap within the UV light absorption spectrum, it is non-toxic, a strong oxidator, and able to degrade organic pollutants within photocatalytic activity [3-6]. To increase the photocatalytic activity of ZnO, modifications using the doping transition metal ferrite (Fe) [7], as well as the addition of zeolite, were performed in our previous work [2]. Zeolite, with its large surface area and high absorption capacity, could also increase the photocatalytic activity of Fe-doped ZnO (Fe:ZnO) [8-10].

Besides increasing photocatalytic activity, a catalyst with good stability also attracts the interest of researchers. It is known that the use of the magnetic material Fe₃O₄ could increase the magnetic



saturation of the sample and enhance the catalyst's stability. Therefore, in this research, the Fe:ZnO/zeolite/Fe₃O₄ nanocomposite was synthesized by using co-precipitation method. Its structural properties, optical properties, magnetic properties, and surface area were also studied. The photocatalytic activity of the nanocomposite, in degrading the methylene blue (MB) as the organic pollutant, was evaluated under UV light radiation. The catalyst's stability was checked after four cycle processes. The main active species in photocatalytic activity was also studied, by adding various scavengers.

2. Experimental details

2.1. Materials

The chemical materials used in this research were purchased from Merck and Sukabumi, Indonesia. Zinc (II) sulfate hepta hydrate (ZnSO₄·7H₂O), iron (II) sulfate hepta hydrate (FeSO₄·7H₂O), sodium hydroxide (NaOH), ethanol, natural zeolite, methylene blue (MB), ethylene glycol, and acetic acid (20%) were analytical grade and used without further purification. Distilled water was used throughout the experiment.

2.2. Synthesis of the Fe:ZnO/Zeolite/Fe₃O₄ nanocomposites

The Fe:ZnO/zeolite nanocomposite and Fe₃O₄ nanoparticles were each synthesized by using co-precipitation [2] and sol-gel [11] method, as described in our previous works. The Fe-doped ZnO/zeolite/Fe₃O₄ (the zeolite amount was held constant by 30 wt.%) nanocomposite was obtained through the following steps: first, the Fe-doped ZnO/zeolite nanocomposite was dissolved into distilled water, while Fe₃O₄ was stirred into ethanol. Then, the two solutions were mixed and ultrasonicated for two hours. A centrifugation process was conducted to separate the precipitations and solutions. Thereafter, the precipitations obtained were allowed to stand at room temperature for 18 hours, before being dried in the oven at 100°C for one hour in vacuum conditions. The Fe-doped ZnO/zeolite/Fe₃O₄ nanocomposite was produced four times, with weight ratios of Fe-doped ZnO/zeolite to Fe₃O₄ of 1:0.05, 1:0.1, 1:0.5, and 1:1, respectively.

2.3. Characterization

The structure, optical properties, magnetic properties, and surface area of the samples were characterized using spectroscopy X-ray diffraction (Rigaku Miniflex 600), fourier transform infrared (FEI Spectrophotometer Shimazu IR Prestige-21), UV-vis diffuse reflectance (Shimadzu UV-Vis spectrophotometer), vibrating sample magnetometer (Oxford type 1.2 T), and Burneur-Emment-Teller (BET).

2.4. Catalytic activity

The photocatalytic activity of the Fe:ZnO/zeolite/Fe₃O₄ nanocomposite was studied using methylene blue (MB) as the model of organic pollutant. A 40 W UV lamp was used as the light irradiation source for the photocatalytic activity. Then, the MB degradation rate was observed for two hours, at intervals of 15 minutes, using a spectrophotometer from UV-Vis Hitachi UH5300. The catalyst's stability was checked after four times cycle processes. The main active species in the degradation process was also observed by adding some materials, such as Na₂S₂O₈, di-ammonium oxalate, and tert-butyl-alcohol, as electrons, holes, and hydroxyl radical scavengers.

3. Results and discussion

XRD spectroscopy was used to study the crystal structure of the synthesized samples. Figure 1a shows the diffraction patterns of the Fe:ZnO/zeolite/Fe₃O₄ nanocomposite sample, with weight ratios of 1:0.05,

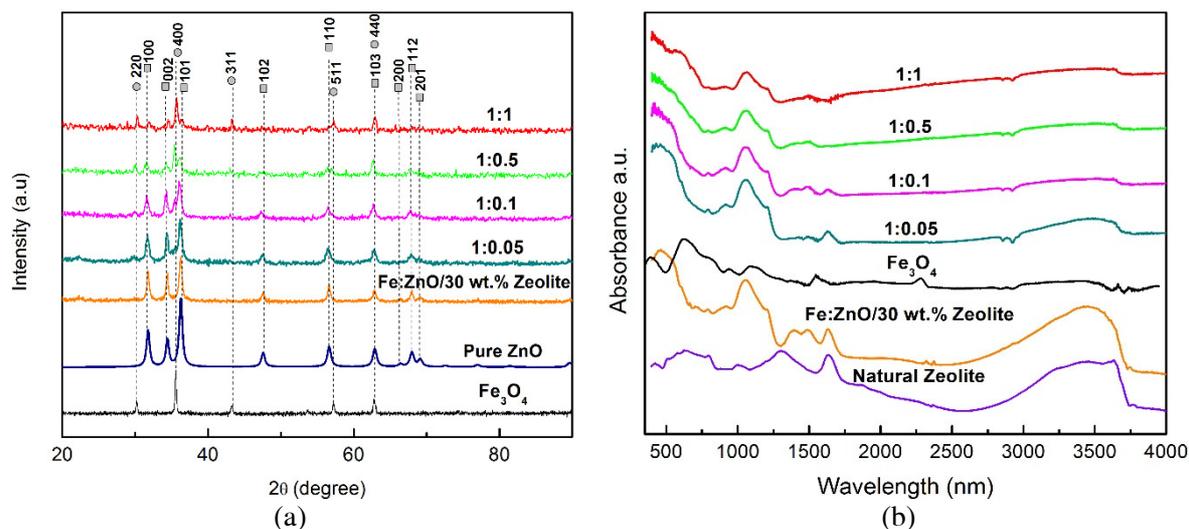


Figure 1. (a) XRD pattern of Fe₃O₄ nanoparticles, ZnO nanoparticles, Fe:ZnO/Zeolite nanoparticles, and Fe:ZnO/Zeolite/Fe₃O₄ nanocomposites; and (b) FTIR spectra of natural zeolite, Fe:ZnO/Zeolite nanoparticles, Fe₃O₄ nanoparticles and Fe:ZnO/Zeolite/Fe₃O₄ nanocomposites.

Table 1. Lattice parameters, unit cell volume, and crystallite size of nanoparticles.

Sample	Weight ratio	Lattice Parameter (Å)			Unit cell volume (Å ³)		Crystallite Size (nm)	
		ZnO a=b	ZnO c	Fe ₃ O ₄ a=b=c	ZnO	Fe ₃ O ₄	ZnO	Fe ₃ O ₄
Fe ₃ O ₄	-	-	-	8.369	-	507.607	-	41
Fe:ZnO/Zeolite	-	3.260	5.191	-	47.775	-	20	-
	1:0.05	3.246	5.183	10.118	47.297	897.212	18	18
Fe:ZnO/Zeolite/ Fe ₃ O ₄	1:0.1	3.247	5.194	12.338	47.419	1626.851	17	21
	1:0.5	3.247	5.195	15.226	47.417	3057.257	13	41
	1:1	3.245	5.191	17.025	47.343	4273.494	11	48

1:0.1, 1:0.5, and 1:1. As comparison, diffraction patterns of the Fe₃O₄ nanoparticle, ZnO nanoparticle, and Fe:ZnO/30 wt.% zeolite nanocomposite can also be seen in the figure. The diffraction pattern of the Fe:ZnO/zeolite/Fe₃O₄ nanocomposite shows the existence of diffraction peaks at $2\theta = 30.36^\circ$, 35.76° , 43.47° , 53.94° , 57.51° , and 63.74° , which represent the areas (220), (311), (400), (442), (511), and (440) that were from the cubic spinel structure of Fe₃O₄ [12], and diffraction peaks at $2\theta = 31.82^\circ$, 34.55° , 36.29° , 47.57° , 56.65° , 62.85° , 66.49° , 67.99° , and 69.13° , which represent the areas (100), (002), (101), (102), (110), (103), (200), (112), and (201) that are from the hexagonal wurtzite ZnO structure [13]. No other phase or impurity was found on the obtained diffraction patterns. The lattice parameter value, obtained by the Rietveld refinement technique using the program MAUD, and the crystal size was calculated through the Debye-Scherrer formula [14], are summarized in table 1.

The presence of zeolite in the sample could be confirmed using FTIR spectroscopy. Figure 1b shows the absorbent spectra of each sample when exposed to infrared at wave numbers of 400-4000 cm⁻¹. The existence of the stretching vibration of Fe-O at wave number 594 cm⁻¹ [15] confirmed the existence of the dopant ion Fe and Fe₃O₄ material in the sample. Meanwhile, the absorption peaks at

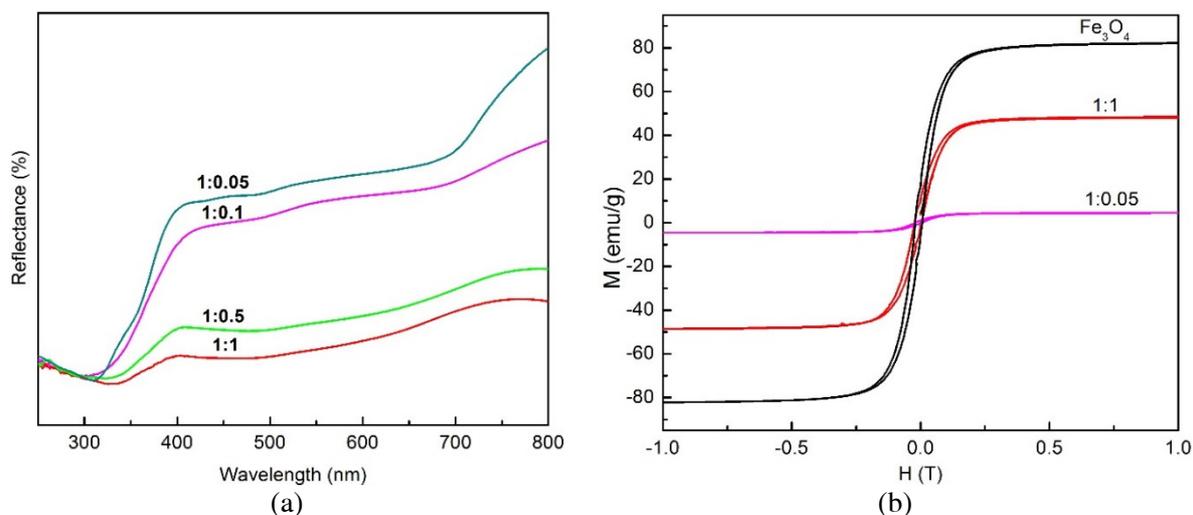


Figure 2. (a) UV-Vis reflectance spectra of Fe:ZnO/Zeolite/Fe₃O₄ nanocomposites; and (b) VSM spectra of Fe₃O₄ nanoparticles and Fe:ZnO/Zeolite/Fe₃O₄ nanocomposites.

Table 2. Band gap and surface area of Fe:ZnO/Zeolite/Fe₃O₄ nanocomposites.

Sample Weight Ratio	Band Gap (eV)	Surface Area (m ² /g)
1:0.05	3.18	82.11
1:0.1	3.15	79.46
1:0.5	3.08	73.99
1:1	3.06	54.01

wave numbers 1049, 1384, and 1723 cm⁻¹, which stemmed from the stretching vibrations of C-O, O-H, and C = O [16]. A vibration mode of the O-H bond at wave numbers 3000-3500 cm⁻¹ [17] was also obtained. The Si-O-Al bending vibration and Si-O-Si stretching vibration were found at wave number 987 cm⁻¹ and 1090 cm⁻¹, respectively, confirm the existence of zeolite in the sample [18, 19].

The reflectance of the UV-Vis measurement result of the Fe:ZnO/zeolite/Fe₃O₄ nanocomposite can also be observed in figure 2a. The band gap value of the samples was obtained by extrapolating the UV-Vis reflectance spectra, using the Kubelka-Munk equation [20]. Table 2 shows the band gap value of the samples. The increasing content of Fe₃O₄ in Fe:ZnO/zeolite decreases the band gap energy of ZnO to the smaller energy (red shift).

The magnetic properties of Fe₃O₄ nanoparticles and Fe:ZnO/zeolite/Fe₃O₄ nanocomposite were measured using VSM spectroscopy. The hysteresis magnetic curve of the samples can be seen in figure 2b. The incorporation of Fe₃O₄ into Fe:ZnO/zeolite, with the ratio 1:1, may have increased the magnetic saturation of the sample to 48.355 emu/g, compared to the magnetic saturation of Fe:ZnO/zeolite/Fe₃O₄ with a ratio of 1:0.05 at 5.97 emu/g. All samples showed ferromagnetic behavior at room temperature, so that, in this research, the separation process of the catalyst from the aqueous organic dye became easier and the stability of the former could also be checked.

Degradation of the organic pollutant model MB, using the Fe:ZnO/zeolite/Fe₃O₄ nanocomposite, was evaluated under UV light irradiation. Figure 3a shows the photocatalytic activity of the nanocomposite, with a different weight ratio of Fe₃O₄. The result obtained shows that the nanocomposite, with a ratio of 1:0.05, displayed maximum degradation of MB. The increase in photocatalytic activity could have been influenced by several factors, including the surface area of the catalyst. The surface area of the Fe:ZnO/Zeolite/Fe₃O₄ nanocomposite is summarized in table 2. The increasing content of Fe₃O₄ in

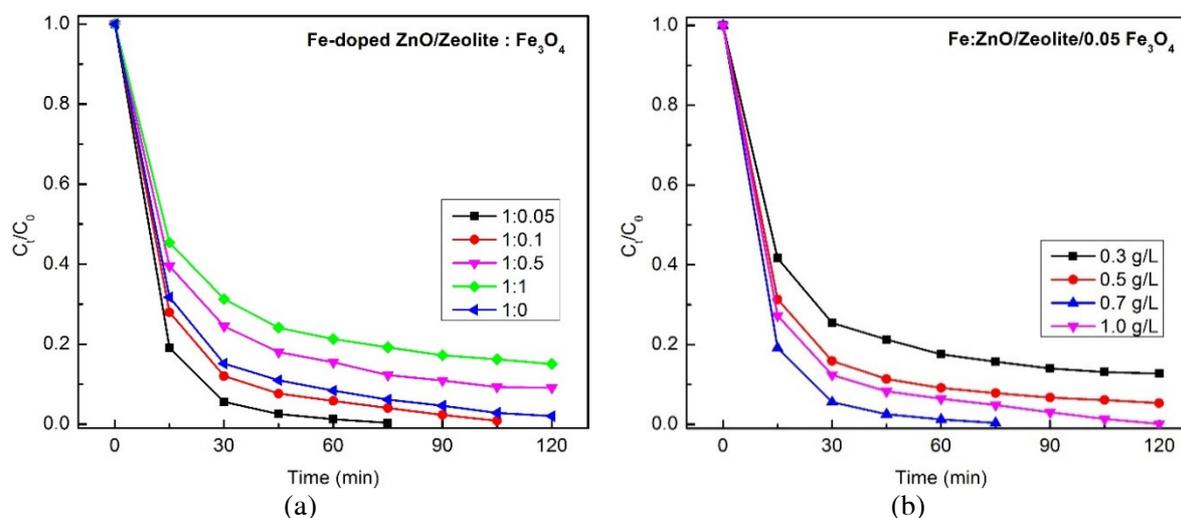


Figure 3. Photocatalytic activity of Fe:ZnO/Zeolite/Fe₃O₄ nanocomposites with various (a) weight ratio of Fe₃O₄; and (b) dosage concentration.

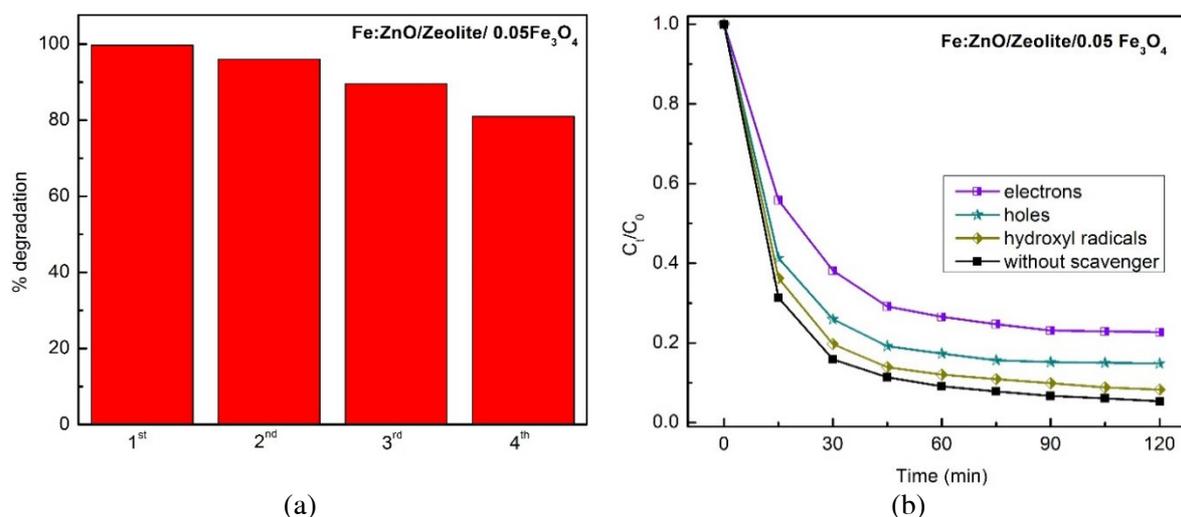


Figure 4. Photocatalytic activity of Fe:ZnO/Zeolite/Fe₃O₄ nanocomposites (a) after 4 cycles processes; and (b) with the effect of scavenger.

Fe:ZnO/Zeolite decreases the surface area value of the catalyst. This result corresponded with the photocatalytic activity obtained. The reduction of the surface area of the catalyst may decrease the contact probability between the catalyst and the MB while irradiated. Therefore, the photocatalytic performance obtained could also decrease accordingly. Figure 3a also shows that the addition of Fe₃O₄ to the Fe:ZnO/zeolite, with ratio of 1:0.05, could enhance the photocatalytic activity of the nanocomposite if compared to Fe:ZnO/zeolite. It is known that the incorporation of Fe₃O₄ in the nanocomposite could also inhibit the recombination rate of the electron and hole, so that the photocatalytic activity obtained also increases more markedly. To ensure optimum conditions in the photodegradation process, the effect of the dosage catalyst has also been evaluated. Figure 3b shows the photocatalytic degradation of MB with various dosage concentrations of the catalyst (Fe:ZnO/zeolite/0.05 Fe₃O₄), from 0.3 g/L to 1.0 g/L. The results show that a 0.7 g/L catalyst is the maximum dosage concentration for degrading MB.

Besides increasing the photocatalytic activity, the advantage of Fe₃O₄ incorporation in the nanocomposite is that it makes the separation process of the catalyst and solutions easier, by using

external magnetism. Then, the separated catalyst was redissolved into a new aqueous MB solution and the photocatalytic activity was rechecked in the same way. The percentage of catalyst degradation after reusing can be seen in figure 4a. The result obtained shows that after four cycles of photocatalytic process, the degradation obtained was decreased, although not significantly. This result indicates that the Fe:ZnO/zeolite/Fe₃O₄ nanocomposite has good stability as a catalyst.

The main active species in the photocatalytic activity was also checked by varying some scavengers. As seen in figure 4b, the addition of tert-butyl alcohol, di-ammonium oxalate, sodium sulfate (Na₂SO₄) as a hydroxyl radical (•OH), holes, and an electron scavenger in a row was able to inhibit the degradation rate of MB. This demonstrates that the main active species in descending order, in this research, was electron > holes > hydroxyl radical (•OH).

4. Conclusions

The Fe:ZnO/zeolite/Fe₃O₄ nanocomposite was successfully synthesized using the co-precipitation method. The photocatalytic activity of Fe:ZnO/zeolite/ Fe₃O₄, with a ratio of 1:0.05, showed higher degradation than Fe:ZnO/zeolite. The incorporation of Fe₃O₄ in the nanocomposite could also increase the magnetic saturation of the sample, so that its stability as a catalyst could be checked in the photocatalytic activity. After four cycles processes, the Fe:ZnO/zeolite/ Fe₃O₄ nanocomposite showed good stability in degrading methylene blue. The main active species in the photocatalytic activity, in descending order, was electron > holes > hydroxyl radical (•OH).

References

- [1] Ruijun C, Kai S, Mingxiang X, Dinghan X and Qingyu Z 2016 *Mater. Sci. Semi. Proc.* **43** 155-62
- [2] Afifah N, Adriani S, Djaja N F and Saleh R 2015 *Adv. Mater. Res.* **1123** 295-302
- [3] Dong S, Xu K, Liu J and Cui H 2011 *Phys. B* **406** 3609-12
- [4] Kumar K, Chitkara M, Sandhu I S, Mehta D and Kumar S 2014 *J. Alloy. Compd.* **588** 681-9
- [5] Hassan M S, Touseef A, Yang O B, Kim H C and Khil M S 2012 *Ceram. Int.* **38** 5925-30
- [6] Anandan S, Vinu A, Mori T, Gokulakrishnan N, Srinivasu P, Murugesan V and Ariga K 2007 *Catal. Commun.* **8** 1377-82
- [7] Saleh R and Djaja N F 2014 *Superlattice. Microst.* **74** 217-33
- [8] Fang L M, Zu X T, Li Z J, Zhu S, Liu C M, Zhou W L and Wang L M 2008 *J. Alloy. Compd.* **454** 261-7
- [9] Corma A and Garcia H 2004 *Chem. Commun.* **13** 1443-59
- [10] Guo Y N, Zu B Y and Dou X C 2013 *J. Thermodyn. Catal.* **4:2** 1000e120
- [11] Taufik I, Susanto K and Saleh R 2015 *Mater. Sci. Forum* **827** 37-42
- [12] Chidambaram S, Pari B, Kasi N and Muthusamy S 2016 *J. Alloy. Compd.* **665** 404-10
- [13] Estévez-Hernández O, Santiago-Jacinto P and Reguera E 2013 *Mater. Focus* **2** 438-42
- [14] Khan M E, Alam F, Parveen A and Naqvi A H 2013 *J. Adv. Microscopy Res.* **8** 45-52
- [15] Chong S, Zhang G, Tian H, Zhao H 2016 *J. Environ. Sci.* **44** 148-57
- [16] Stankovich S, Piner R D, Nguyen S T and Ruoff R S 2006 *Carbon* **44** 3342-7
- [17] Xing S, Zhou Z, Ma Z and Wu Y 2011 *Appl. Catal. B* **107** 386-92
- [18] Du E, Yu S, Zuo L, Zhang J, Huang X and Wang Y 2011 *Appl. Clay Sci.* **51** 94-101
- [19] Chen D, Honglei Z and Wang X 2014 *Appl. Surf. Sci.* **319** 158-66
- [20] Lavand A B and Malghe Y S 2015 *J. Saudi Chem. Soc.* **19** 471-8