Journal of Ceramic Processing Research. Vol. 16, No. 5, pp. 457~461 (2015)

J O U R N A L O F
Ceramic Processing Research

Photocatalytic activities of carbon nanocapsules encircled by nickel nanoparticle composites to organic dyes degradation

Jiulong Li[a], Jeong Won Ko[a] and Weon Bae Ko[a,b,*]

[a]*Department of Convergence Science, Graduate School, Sahmyook University, Seoul 139-742, South Korea*
[b]*Department of Chemistry, Sahmyook University, Seoul 139-742, South Korea*

Novel carbon nanocapsules encircled by nickel nanoparticle composites were prepared by the reaction of fullerene[C_{60}] and nickel hydroxide at 700 °C for 2 h. Carbon nanocapsules encircled by nickel nanoparticle composites were characterized by X-ray diffraction, Raman spectroscopy, scanning electron microscopy and transmission electron microscopy. It may be confirmed the structure of fullerene[C_{60}] changed into capsule like type of carbon nanomaterials and nickel nanoparticles were surrounded by carbon nanocapsules by HR-TEM. Application of carbon nanocapsules encircled by nickel nanoparticle composites could be used as a photocatalyst in the degradation of organic dyes under ultraviolet light at 254 nm.

Key words: Carbon nanocapsules encircled by nickel nanoparticle composites, Raman spectroscopy, HR-TEM, Photo catalytic degradation.

Introduction

Nano carbon materials have been researched to a large extent as a photo catalyst due to their outstanding structural properties and amendable chemical natures [1-3]. The concern of carbon nanomaterials with nickel has increased in recent years, as nickel was found to be an efficient catalyst for the formation of carbon nanotubes and fibers at elevator temperatures [4]. Nickel, the magnetic nanoparticles were synthesized and applied on ferro fluids [5], data storage [6], catalysis [7], environmental protection [8], magnetic resonance imaging as contrast agents [9], as well as field-oriented drug delivery system [10, 11]. Carbon nanomaterials seem to be useful for encapsulation, because the high stability in both physical and chemical environments that effectively prevent the agglomeration and high surface activity [12, 13]. Fullerene[C_{60}] whose atoms are arranged in closed hollow shells, show relatively weak electron acceptor properties and form mainly molecular complexes with metal-free and no noticeable charge transfer in the ground state [14]. However in our work, fullerene[C_{60}] was changed capsules like type of carbon nanomaterials by nickel hydroxide at 700 °C and combine with nickel nanoparticles. This new products were seemed to be amorphous type of carbon-nickel nanocomposites. Raman spectroscopy as an extremely useful technique to characterize carbon nanomaterials was used to characterize amorphous carbon-nickel nanocomposites [15]. X-ray diffraction, scanning electron microscopy and transmission electron microscopy were also used to characterize the structure of carbon nanocapsules encircled by nickel nanoparticle composites.

In this paper, the photocatalytic reactions were showed at the degradation of organic dyes such as methylene blue, rhodamine B, brilliant green and methyl orange under ultraviolet light at 254 nm by UV-vis spectrophotometer.

Experimental

Materials and Instruments

Nickel (II) acetate tetrahydrate [$Ni(CH_3COO)_2 \cdot 4H_2O$], sodium hydroxide (NaOH), ethanol (C_2H_5OH), tetrahydrofuran (THF), methylene blue (MB) were purchased from Samchun Chemicals (Korea). Brilliant green (BG), methyl orange (MO) and rhodamine B (RhB) were obtained from Sigma-Aldrich (Korea). Fullerene[C_{60}] was supplied by Tokyo Chemical Industry Co., Ltd.

Microwave irradiation was performed to handle the mixture at the maximum power in a domestic oven (2450 MHz, 700 W). The sample was heated by an electric furnace (Ajeon Heating Industry Co., Ltd). The structure of carbon nanocapsules encircled by nickel nanoparticle composites was examined by X-ray diffraction (XRD, Bruker, D8 Advance). The surface of sample was observed by scanning electron microscopy (SEM, JEOL Ltd, JSM-6510) at an accelerating voltage of 0.5 to 30 kV. Transmission electron microscopy (TEM, JEOL Ltd, JEM-2010) at an acceleration voltage of 200 kV was used to investigate morphology and size of carbon nanocapsules encircled by nickel nanoparticle composites. Raman spectroscopy was used

*Corresponding author:
Tel : +82-2-3399-1700
Fax: +82-2-979-5318
E-mail: kowb@syu.ac.kr

to characterize for carbon nanocapsules encircled by nickel nanoparticle composites. The irradiated light source was an UV lamp (8 W, 254 nm, 77202 Marne La Valee-cedex 1 France). The activity of photocatalytic degradation was evaluated by UV-vis spectrophotometer (Shimazu UV-1619PC).

Material Synthesis

Preparation of nickel hydroxide

In order to obtain nickel hydroxide powder, nickel (II) acetate tetrahydrate and sodium hydroxide were dissolved in ethanol with a mole ratio of 1 : 2. After stirring for 4 h at room temperature with magnetic stirrer, the beaker containing of the mixture solution was irradiated under microwave irradiation for 5 min (15 s, 20 times). The obtained sample was washed 5 times with an ethanol solution (the volume ratio of ethanol : water = 1 : 1) to remove the impurities and then dried at 80 ºC overnight in an electric oven. Nickel hydroxide, a green powder was gained as a product.

Preparation of carbon nanocapsules encircled by nickel nanoparticles

The carbon nanocapsules encircled by nickel nanoparticle composites were prepared by nickel hydroxide powder and fullerene[C_{60}] with a mass ratio of 2 : 1. Two substances which were mixed in tetrahydrofuran by stirring and then heated in an electric furnace to 700 ºC under an atmosphere of inert argon gas for 2 h. After the products were cooling down to room temperature, black particles were obtained.

Characterization of materials

XRD patterns were obtained by X-ray diffraction with Cu Kα radiation. Morphology of product was observed by SEM and the size of carbon nanocapsules encircled by nickel nanoparticle composites were characterized by TEM. Raman spectroscopy as a useful technique to characterize carbon nanomaterials was combined to examine the property of the product by analyzing the peak of D-band, G-band and 2D-band.

Measurement of photocatalytic activity

In the photocatalytic experiment, the carbon nanocapsules encircled by nickel nanoparticle composites were used to test the degradation of organic dyes such as MB, RhB, BG and MO. 5 mg of carbon nanocapsules encircled by nickel nanoparticle composites were added in 10 ml of each organic dye solution. The vessel containing the mixture was irradiated by an UV-lamp with the wavelength of 254 nm light. UV-vis spectrophotometry was used to analyze the photocatalytic degradation of organic dyes.

Result and Discussion

Characterization of carbon nanocapsules encircled by nickel nanoparticle composites

The X-ray diffraction pattern of the carbon nanocapsules encircled by nickel nanoparticle composites was shown in Fig. 1.

The peaks of carbon nanocapsules encircled by nickel nanoparticle composites were observed at 26.3 º, 44.4 º, 51.8 º and 76.3 º as a 2θ value. The XRD pattern indicated that the crystal structure of carbon nanocapsules encircled by nickel nanoparticle composites was different as compared to the pure fullerene[C_{60}] powder, which was shown in Fig. 2.

As shown in Fig. 1, the peaks located at 44.4 º, 51.8 º and 76.3 º as a 2θ value were proved to be the three plane index of Ni (111), (200) and (220), respectively (JCPDS4-850) [16, 17]. The other peak at 26.3 º was deduced to the indice of carbon nanocapsules composites [16-18]. As we can be seen on Fig. 3.

D-band discovered around 1338 cm^{-1} and G-band discovered around 1570 cm^{-1} were observed in Raman spectra. D-band is due to carbonaceous impurities or graphite structural defect while G-band is due to graphitized to graphite crystal [19, 20].

Amorphous carbon nanomaterials can be calculated according to the height ratio of D-band / G-band. The value ratio of D /G band was less than 1, therefore, carbon nanocapsules composites seemed to be an amorphous carbon nanomaterial. Also, 2D-band observed around 2676 cm^{-1} due to graphene [21]. Raman shift data

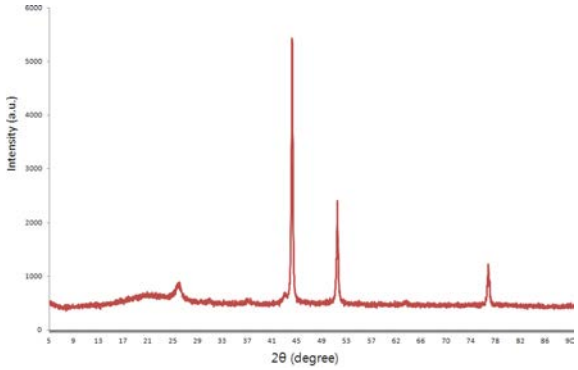

Fig. 1. XRD pattern of carbon nanocapsules encircled by nickel nanoparticle composites.

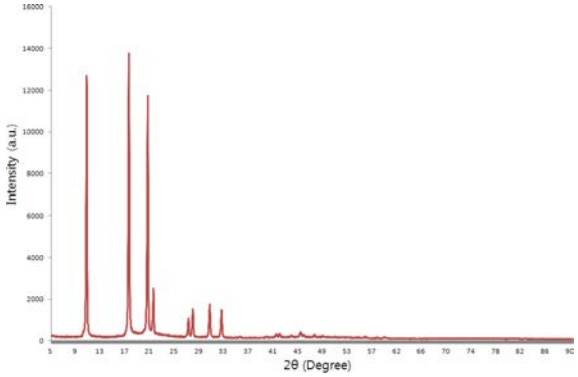

Fig. 2. XRD pattern of pure fullerene [C_{60}] nanoparticles.

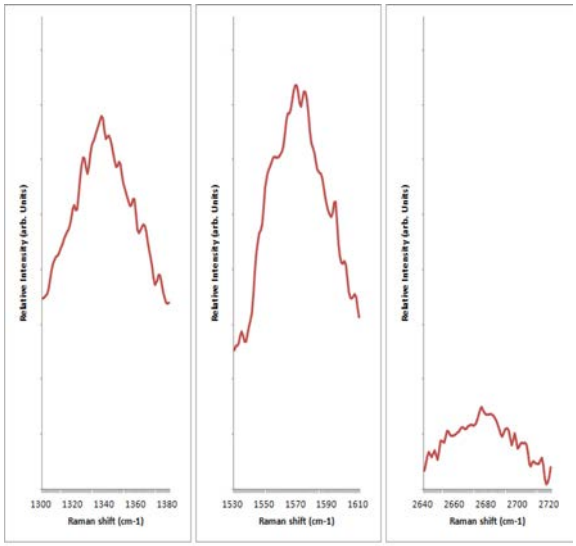

Fig. 3. Raman spectra of the carbon nanocapsules encircled by nickel nanoparticle composites; (a) is D-band, (b) is G-band, (c) is 2D-band.

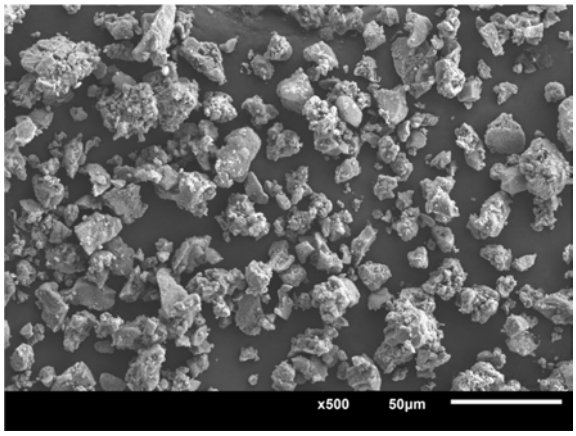

Fig. 4. SEM image of the carbon nanocapsules encircled by nickel nanoparticle composites.

may be present the carbon nanocapsules encircled by nickel nanoparticles in the carbon nickel nanocomposites. The image of SEM were showed in Fig. 4.

The image revealed a stone-like morphology with clastic deposit sticked on its surface. The information of the surface is formed during the incorporation of nickel in carbon nanocapsules. Fig. 5(a) and (b) showed TEM images of the nanocomposites with a core-shell structure.

The nickel particles were encapsulated by carbon nanocapsules which was displayed as elliptic shape in Fig. 5(a). The mean diameter of carbon nanocapsules encircled by nickel nanoparticle composites was about 50 nm. At a higher magnification by HR-TEM in Fig. 5(b), the nickel particles were surrounded by amorphous carbon with a lattice fringes appearance. The interlayer distance between amorphous carbon was approximately 0.3 nm [4, 11].

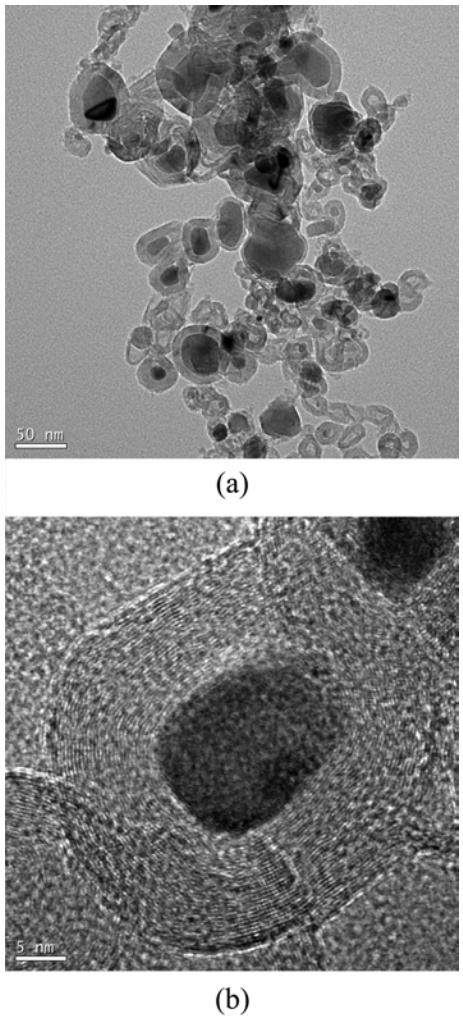

Fig. 5. TEM images of the carbon nanocapsules encircled by nickel nanoparticle composites.

Photocatalytic Degradation of Organic Dyes

Fig. 6 showed the UV-vis spectra of the degradation of (a) MB, (b) RhB, (c) BG and (d) MO with carbon nanocapsules encircled by nickel nanoparticle composites as a photocatalyst under ultraviolet irradiation at 254 nm.

The nickel nanoparticles were encapsulated with carbon nanocapsules which were showed excellent photocatalytic activity and stability because it may be changed the band gap between conduction band (CB) and valence band (VB) [22-24]. When carbon nanocapsules encircled by nickel nanoparticle composites were irradiated by the UV-lamp at 254 nm, the electron (e^-) transferred from valence band to conduction band due to the influence of carbon nanomaterials which were carbon nanocapsules. Spectra in Fig. 6(a)-(d) indicated that the organic dyes were degraded by the effect of the carbon nanocapsules encircled by nickel nanoparticle composites under ultraviolet light at 254 nm. It may be ascribed the smaller band gap energy of carbon nanocapsules encircled by nickel nanoparticle composites.

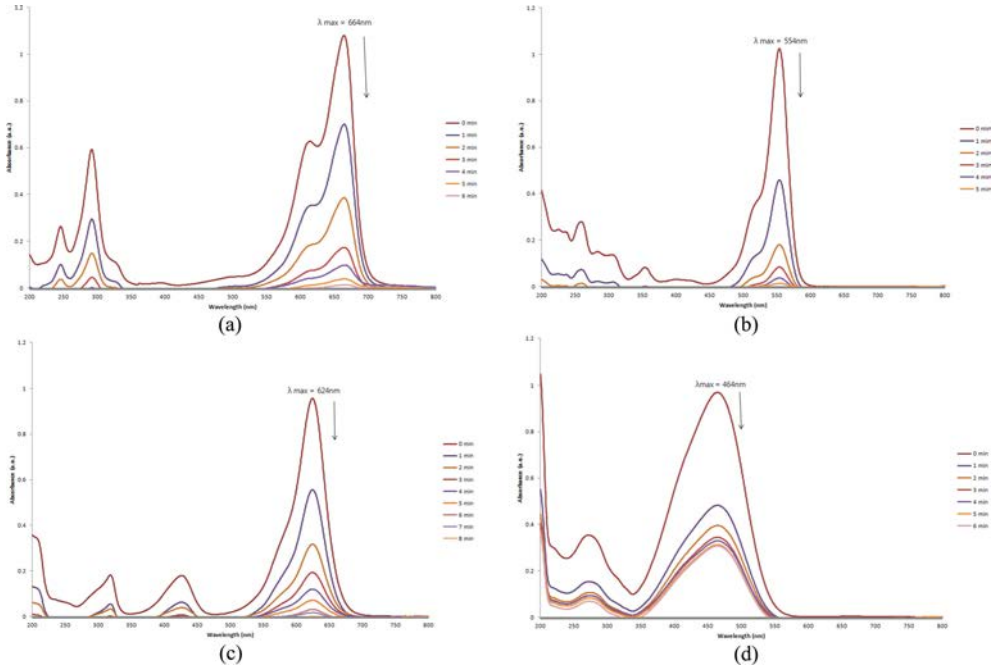

Fig. 6. UV-vis spectra of the degradation of (a) MB, (b) RhB, (c) BG and (d) MO with the carbon nanocapsules encircled by nickel nanoparticle composites as a photocatalyst under ultraviolet irradiation at 254 nm.

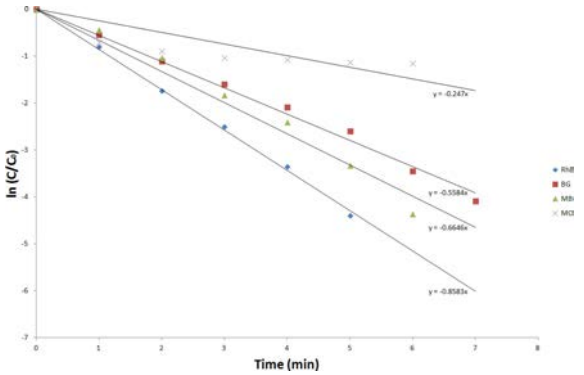

Fig. 7. Kinetic study of the degradation of the organic dyes such as (a) MB, (b) RhB, (c) BG and (d) MO.

Table 1. The value of concentration ratio (ln C/C_0) in the photocatalytic degradation of organic dyes according to the time.

Time (min)	RhB (lnC/C_0)	BG (lnC/C_0)	MB (lnC/C_0)	MO (lnC/C_0)
0	0	0	0	0
1	–0.8035	–0.5432	–0.4337	–0.6981
2	–1.7410	–1.1040	–1.0295	–0.8966
3	–2.5065	–1.6006	–1.8315	–1.0347
4	–3.3518	–2.0822	–2.4116	–1.0801
5	–4.3988	–2.6011	–3.3280	–1.1331
6		–3.4494	–4.3669	–1.1496
7		–4.0850		

Kinetic study of photocatalytic degradation of organic dyes

In the photocatalytic reactions, the concentration of the carbon nanocapsules encircled by nickel nanoparticle composites as a catalyst was used at 500 mg/L according to the volume of organic dyes solution. Fig. 7 revealed that the degradation of the organic dyes followed a pseudo-first-order rate law.

It meant that the rate of degradation almost can be seen as a constant line. Langmuir-Hinshelwood model has been applied on the kinetic of many organic compounds [25]. So the equation can be written as follows:

$$\ln (C/C_0) = -kt$$

In which C_0 was the initial concentration of dyestuff solution, C was the concentration at measuring time t and k is the rate constant. Table 1 lists kinetics of the photocatalytic degradation of MB, RhB, BG and MO by first-order reaction which is kinetics equation.

The order of the kinetics of the photocatalytic degradation of the organic dyes were RhB > MB > BG > MO.

Conclusions

In our study, carbon nanocapsules encircled by nickel nanoparticle composites were synthesized with fullerene [C_{60}] and nickel hydroxide. Carbon nanocapsules encircled by nickel nanoparticle composites were observed at 26.3 °, 44.4 °, 51.8 ° and 76.3 ° as a 2θ value by XRD. In Raman spectra, we can be observed D-band (1338 cm^{-1}), G-band (1570 cm^{-1}) and 2D-band (2676 cm^{-1}). From the images of SEM and TEM, we knew the carbon nanocapsules encircled by nickel nanoparticle composites have a stone-like morphology with clastic deposit sticked

on its surface and the mean diameter of particles was about 50 nm. In the photocatalytic reaction, carbon nanocapsules encircled by nickel nanoparticle composites were used for degradation of various organic dyes such as MB, RhB, BG and MO at 254 nm. The order of photocatalytic degradation is the following of this; RhB MB BG MO. In addition, kinetic study of photocatalytic degradation with carbon nanocapsules encircled by nickel nanoparticle composites followed a pseudo-first-order reaction.

Acknowledgments

This study was supported by Sahmyook University research funding in Korea.

References

1. K. Dai, G. Dawson, S. Yang, Z. Chen and L. H. Lu, *Chem.Eng.J.*, 191 (2012) 571-578.
2. R. Leary and A. Westwood, *Carbon*, 49 (2011) 741-772.
3. S. Z. Kang, L. L. Chen, X. Q. Li and J. Mu, *Appl. Surf. Sci*., 258 (2012) 6029-6033.
4. R. Anton, *Carbon*, *46* (*2008*), 656-662.
5. U. Jeong, X. Teng, Y. Wang, H. Yang and Y. Xia, *Adv. Mater.*, 19 [1] (2007) 33-60.
6. G. Reiss, A. Hutten, *Nat. Mater*., 4 [10] (2005) 725-726.
7. A. R. Herdt, B. S. Kim and T. A. Taton, *Bioconjugate Chem.*, 18 [1] (2007) 183-189.
8. M. Bystrzejewski, K. Pyrzynska and A. Huczko et al., *Carbon*, 47 (2009) 1189-1206.
9. C. S. Wang, X. N. Wang, S. W. Anderson and X. Zhang, *Sensor. Actuat. B Chem., B.* 196 (2014) 670-675.
10. M. Bystrzejewski, Z. Karoly, J. Szepvolgyi, W. Kaszuwara, A. Huczko and H. Lange, *Carbon,* 47 (2009) 2040-2048.
11. C. Ma, B. Luo, H. H. Song and L. J. Zhi, *New Carbon Mater*., 25 [3] (2010) 199-204.
12. K. Kobayashi, H. Ueno, K. Kokubo, M. Yudasakas and H. Yasuda, *Carbon*, 68 (2014) 346-351.
13. Z. P. Xu, Q. H. Zeng and G. Q. Lu et al., *Chem. Eng. Sci*., 61 (2006) 1027-1040.
14. D. V. Konarev, S. S. Khasanov and R. N. Lyubovskaya, *Coord. Chem. Rev.*, 262 (2014) 16-36.
15. A. Righi, P. Venezuela, H. Chacham, S. D. Costa, C. Fantini, R. S. Ruoff, L. Colombo, W. S. Bacsa and M. A. Pimenta, *Solid State Commun*., 175-176 (2013) 13-17.
16. T. Sreethawong, S. Chavadej, S. Ngamsinlapasathian, and S. Yoshikawa, *Colloid Surf. A-Physicochem. Eng. Asp*., 296 (2007) 222-229.
17. X. F. Li, A. Dhanabalan and C. L. Wang, *J. Power Sources*, 196 (2011) 9625-9630.
18. M. Sathish, K. Miyazawa and T. Sasaki, Diam. Relat. Mater., 17 (2008) 571-575.
19. R. W. Havener, S. Y. Ju, L. Brown, Z. H. Wang and M. Wojcik, J. Park etal., *ACS Nano*, 6 [1] (2012) 373-380.
20. A. Righi, S. D. Costa, H. Chacham, C. Fantini, P. Venezuela, C. Magnuson, L. Colombo,W. S. Bacsa, R. S. Ruoff and M. A. Pimenta, *Phys. Rev. B*, 84 (2011) 241409 (R).
21. P. Venezuela, M. Lazzeri and F. Mauri, *Phys. Rev. B*, 84 (2011) 035433.
22. T. Y. Peng, X. H. Zhang, P. Zeng, K. Li, X. G. Zhang and X. G. Li, *J. Catal*., 303 (2013) 156-163.
23. A. H. Lu, E. L. Salabas and F. Schuth, *Angew. Chem. Int. Ed.*, 46 (2007) 1222-1244.
24. X. G. Liu, B. Li, D. Y. Geng, W. B. Cui, F. Yang, Z. G. Xie, D. J. Kang and Z. D. Zhang, *Carbon*, 47 (2009) 470-474.
25. M. A. Behnajady, N. Modirshahla and R. Hamzavi, *J. Hazard. Mater. B*, 133 (2006) 226-232.