

Preparation of Co-ACFs/TiO₂ composites and its photodegradation of methylene blue

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Co-ACFs/TiO₂ 복합체의 제조 및 그의 메틸렌블루의 광분해

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Abstract Cobalt-loaded activated carbon fibers (ACFs) supported titanium dioxide (TiO₂) photocatalyst was developed by sol-gel method. The Co-ACFs/TiO₂ photocatalyst were characterized by scanning electron microscope (SEM), X-ray diffraction patterns (XRD), energy dispersive X-ray analysis (EDX) and UV-vis absorption spectroscopy. Decomposition efficiency of methylene blue (MB) solution by Co-ACFs/TiO₂ photocatalyst reached almost 100% under 300 min reaction. The MB molecules in the bulk solutions were supposed to be condensed around TiO₂ particles by adsorption of ACFs. Therefore, the photocatalyst possesses the combined effect of adsorption by activated carbon fibers and photocatalytic reactivity of TiO₂ on MB degradation. Due to the cobalt has electron transition effect, thus improved the photodegradation of MB solution.

요 약 코발트 적재된 활성탄소섬유(ACFs)는 이산화티탄(TiO₂) 광촉매 반응을 촉진시키는 것을 발견되었다. Co-ACFs/TiO₂ 광촉매는 SEM, XRD, EDX 및 UV-vis 분광기를 사용하여 분석하였다. Co-ACFs/TiO₂ 광촉매에 대한 메틸렌블루(MB)의 분해 효과는 300분 반응해서 거의 100%를 도달하였다. 용액에 있는 MB 분자들은 ACFs의 흡착에 의해 TiO₂ 입자의 주위에 응축한다고 가정되었다. 그래서 이 광촉매 복합체는 MB 광분해에 대한 활성탄의 흡착성과 TiO₂의 광촉매 특성의 결합한 성능을 가지고 있다. 코발트가 전자 천이 효과를 가지고 있기 때문에 MB 용액의 광분해가 증가되는 것으로 판단된다.

Key Words : Titanium n-butoxide, activated carbon fibers, photocatalysis, methylene blue

1. Introduction

As representation of heterogeneous photocatalytic oxidation, titanium dioxide (TiO₂) is a promising material for removal of organic pollutants presented in wastewater [1]. Under ultraviolet (UV) irradiation, electron/hole pairs are excited in valence band of TiO₂ and then migrate to the surface to initiate redox reactions for adsorbed organic

pollutants. The concentration of organic pollutants around TiO₂, has a great effect on decomposition rate. Moreover, mineralization of organic pollutants is a result of continuous photocatalysis process, and many intermediate species with higher toxicity are formed during organic pollutant decomposition. Catherine and co workers reported that benzaldehyde and benzoic acid were formed during the photocatalysis of toluene [2]. Therefore,

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Received April 20, 2009

Revised (1st September 24, 2009, 2nd November 9, 2009)

Accepted November 12, 2009

composition with titanium dioxide as photocatalyst and support materials with large surface area would be of great significance. Recently, several works applied this idea for water remediation [3-5]. The pollutants concentrated on the support materials migrated to the surface of TiO₂ by diffusion and then were decomposed. ACFs are a new kind of microporous activated carbon consisting of disordered nanographites. Compared with conventional adsorbent material such as activated carbon (AC), ACFs has larger adsorption capability and faster adsorption rate [6]. As the micropore sizes are about 1~2 nm, the TiO₂ particles with crystal size of twenties nm are adsorbed only on the external surface of ACFs [7]. ACFs are especially helpful for the removal of pollutants in familiar domestic wastewater with molecular weight in the range of 50~300. Micropores are directly opened on the external surface of ACFs, resulting in the larger adsorption capacity and faster desorption rates. Due to the particular property of ACFs including large specific surface area, pore volume, uniform microporosity and high adsorption and desorption rates, it was chosen as support of TiO₂ catalyst in this work. However, ACF have disadvantages in common, such as poor selectivity, poor adsorption of lower boiling point gases, etc [8]. Much attention has been paid on how to tailor the ACFs for selective and/or enhanced removal of specific contaminants. It was also reported that the transition metal compounds, including Co, Ni, Fe, and metals of the Pt group, are known to form metal ion - aromatic complexes of different compositions [9], and could form coordination compound with chlorine [10, 11] through free d orbit of metal and isolated electron pair. The adsorption property of compound containing chlorine should be improved when metal compound was loaded on porous carbon because the adsorption and chemical interaction were connected.

In this present work, ACFs re-treated by cobalt chloride (CoCl₂) was selected as an adsorptive support for TiO₂ loading. The Co-ACFs/TiO₂ composites were prepared by sol-gel method using titanium *n* butoxide (TNB) as precursor, following by heat treatment at suitable temperature. The Co-ACFs/TiO₂ composites were characterized by SEM, XRD and EDX. To determine the photocatalytic decomposition of the composites, methylene blue (MB) was chosen as the model pollutant

under UV irradiation.

2. Experimental

2.1 Materials

TNB (99.9%) was purchased from Acros organics Co., Ltd, USA, as the titanium source. ACFs were purchased from EAST ASIS Carbon Fibres Co., Ltd, AnShan, China. The properties of ACFs were shown at Table 1. The cobalt chloride (CoCl₂) which used to modify the ACFs, were obtained from Duksan Pure Chemical Co., Ltd, Korea. Benzene (99.5%) was used as organic solvents which were purchased from Samchun Pure Chemical Co., Ltd, Korea. The methylene blue (MB, C₁₆H₁₈N₃S·Cl·3H₂O) was used as analytical grade which was also obtained from Duksan Pure Chemical Co., Ltd, Korea.

[Table 1] The properties of ACFs

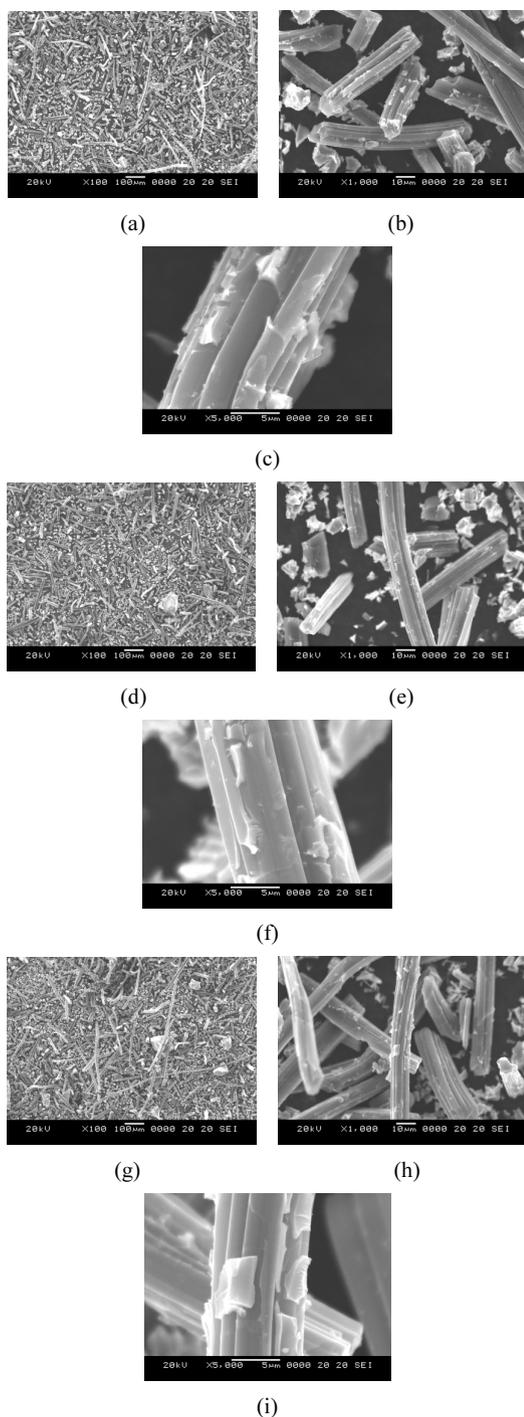
Physical properties	Units
Density	1.23~1.91 g/mL
Electrical Resistivity	$5.2 \times 10^{-3} \sim 6.8 \times 10^{-3} \Omega \cdot \text{cm}$
Diameter	12~15 μ
Tensile Strength	$4 \sim 6 \times 10^8 \text{ Pa}$
Tensile Modulus	$3 \times 10^{10} \sim 4 \times 10^{10} \text{ Pa}$
Elemental carbon	$\geq 95 \text{ wt\%}$

[Table 2] Nomenclatures of Co-ACFs/TiO₂ composites prepared with TNB and cobalt chloride modified ACFs

Samples	Nomenclatures
0.01 M CoCl ₂ treated ACF + TNB : Benzene (50 : 50)	CAT1
0.05 M CoCl ₂ treated ACF + TNB : Benzene (50 : 50)	CAT2
0.1 M CoCl ₂ treated ACF + TNB : Benzene (50 : 50)	CAT3

2.2 Preparation of Co-ACFs/TiO₂ composites

For the preparation of composites, 5.0 g ACFs were milled to powders. Then the ACFs powders were boiled in 100 mL 0.01 M, 0.05 M and 0.1 M CoCl₂ solution at 333 K for 3 h, respectively. Cobalt chloride modified ACF (Co-ACF) powders were dried at 378 K. The dried Co-ACFs powders were mixed



[Fig. 1] SEM images of Co-ACFs/TiO₂ composites prepared with TNB and cobalt chloride modified ACFs;

CAT1: (a) $\times 100$, (b) $\times 1000$ and (c) $\times 5000$; CAT2: (d)

$\times 100$, (e) $\times 1000$ and (f) $\times 5000$; CAT3: (g) $\times 100$, (h) $\times 1000$ and (i) $\times 5000$.

in a mixing solution of TNB and benzene with a regular ratio of 50:50, stirring at 343 K for 5 h in an airtight container. After the stirring the solutions were transformed to the Co-ACFs and TiO₂ mixed gels, and these gels were heat treated at 973 K for 1 h with a heating rate of 279 K/min. The preparation condition and code of samples were listed in Table 2.

Synthesized powders were characterized by various techniques. SEM was used to observe the surface state and structure of the Co-ACFs/TiO₂ composites. The analyses were carried out by using a JSM 5200 JOEL electron microscope (Japan). XRD was used for crystal phase identification and estimation of the anatase-to-rutile ratio. XRD patterns were obtained at room temperature with a Shimata XD D1 (Japan) using CuK α radiation. EDX was used to measure the elemental analysis of the Co-ACFs/TiO₂ composites. UV-vis spectra for the MB solution degraded by Co ACFs/TiO₂ composites under UV lamp irradiation were recorded using a Genspec III (Hitachi, Japan) spectrometer.

2.3 Photocatalytic decomposition for MB solution

The photocatalytic effects of Co-ACFs/TiO₂ composites were determined using MB decomposition in aqueous solution under an UV lamp (356 nm, 1.2 mW/cm²). According to former works [12, 13], the initial MB concentration was chosen 1.0×10^{-5} mol/L, and the amount of suspended composites was kept at 1 g/L in 50 mL MB solution. The solution was irradiated with UV. Samples were then withdrawn regularly from the reactor by an order of 30 min, 90 min, 150 min and 300 min, and immediately centrifuged to separate any suspended solid. The clean transparent solution was analyzed by a UV vis spectrophotometer [14, 15]. The spectra (550-750 nm) for each sample were recorded and the absorbance was determined at characteristic wavelength 660 nm for the each MB solution degraded.

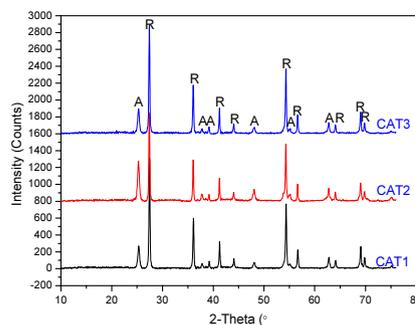
3. Results and Discussion

3.1 Morphology and structure of Co-ACFs/TiO₂ composites

SEM micrographs in Fig. 1 show the morphology of Co-ACFs/TiO₂ photocatalysts. The low magnifications of Fig. 1 show TiO₂ coating has been immobilized onto almost each fiber of ACFs. Although TiO₂ coating has been deposited on carbon fibers as such a large scale, Fig. 1 show TiO₂ still retains Fig. 1 same spatial distribution as that of the original carbon fibers. Therefore, adequate UV irradiation can penetrate sufficiently deep into the photocatalyst felt to form a three dimensional for photocatalytic reaction. This feature differentiates the present photocatalyst from such current immobilizing photocatalysts as immobilized TiO₂ on the surfaces of glass substrates [16], silica gel [17], steel plate [18] or ceramic membrane [19], which could provide only two-dimensional surfaces for photodegradation. From the higher magnifications of Fig. 1, we can see that the surface of Co-ACFs/TiO₂ composites is rough and contains defects, which caused by introduction of Co particles and TiO₂ particles during modification. Furthermore, due to shrinkage of the hydroxylated titania coating during calcinations at elevated temperatures, part of the resulting TiO₂ layer on the carbon fibers is split into flakes, as shown in Fig. 1 (c), (f) and (i).

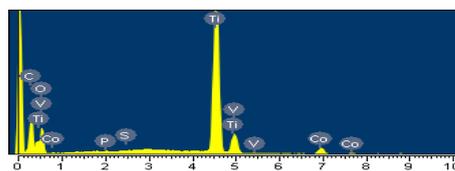
It is well known that the crystal structure of the titanium dioxide is mainly determined by the heat treatment temperature. Since the cobalt was impregnated using cobalt chloride and calcinated at 973 K, the chemical state of cobalt was deduced to be chloride or metal. However, it cannot be detected by XRD, as can be seen in Fig. 2. According to the former study [20], it was known that the anatase phase formed below 773 K began to transform to rutile-type structure above 873 K and changed into single phase of rutile at 973 ~1173 K. The peaks at 25.3, 37.8, 48.0, 53.8, 54.9 and 62.5 are the diffractions of (101), (004), (200), (105), (211) and (204) planes of anatase, indicating the developed composites existed in anatase state. There are some peaks also found at 27.4, 36.1, 41.2 and 54.3 that belong to the diffraction peaks of (110), (101), (111) and (211) of rutile. Therefore, it can be concluded that the developed Co-ACFs/TiO₂ composites have a mixture crystal structure, just is anatase and rutile structures. It is agreed

with the previous works [21, 22] which prepared C/TiO₂ composites had a mixture structure of anatase and rutile crystals by crystallization when the temperature reached 973 K.

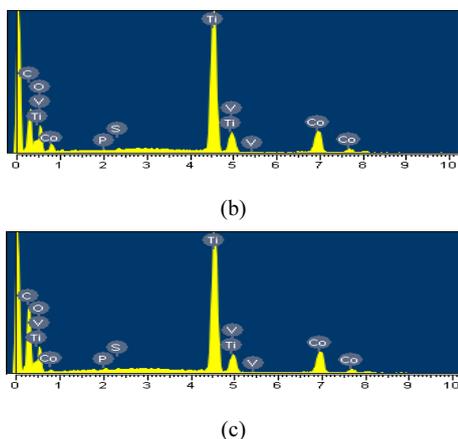


[Fig. 2] XRD patterns of Co-ACFs/TiO₂ composites prepared with TNB and cobalt modified ACFs with heat treatment at 973 K for 1 h.

The EDX spectra of Co-ACFs/TiO₂ composites are shown in Fig. 3. From the spectra, all of the Co-ACFs/TiO₂ composites show the main peaks of C, O and Ti, though a few of impure elements such as P are existed (which may be introduced from experimental procedure). So it is attested that the Co-ACFs/TiO₂ composites were formed and contained these three main elements. The EDX elemental microanalysis (wt. %) of Co-ACFs/TiO₂ composites is listed in Table 3. From the data, we can also see that all of the samples are rich in C, O and Ti elements with a very poor in impure elements. It can be explained the appearance from their SEM observations as mentioned above. On the other hand, it is noticed that the amount of C element of all samples is much more than the amount of Ti and O elements.



(a)



[Fig. 3] EDX elemental microanalysis of Co-ACFs/TiO₂ composites prepared with TNB and cobalt chloride modified ACFs; (a) CAT1, (b) CAT2 and (c) CAT3.

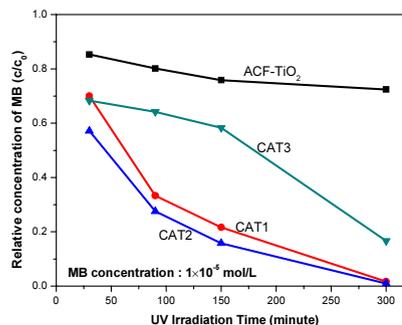
[Table 3] EDX elemental microanalysis (wt.%) of Co-ACFs/TiO₂ composites prepared with TNB and cobalt chloride modified ACFs

Samples	Elements				
	C	O	Ti	Co	Others
CAT1	18.6	35.0	39.9	5.92	0.58
CAT2	22.4	31.9	35.9	8.95	0.86
CAT3	31.2	22.5	31.9	13.9	0.50

3.2 Photocatalytic activity of Co-ACFs/TiO₂ composites

Decomposition ability of Co-ACFs/TiO₂ system was studied through evaluating the decomposition rate of MB. All the tests were conducted under the same conditions so as to compare the performance of different samples. Intensity of the absorption spectrum at $\lambda=660$ nm corresponded to the concentration of MB solution. The curves of MB decomposition under UV irradiation are presented in Fig. 4. It can be clearly seen that the cobalt no-treated sample (ACF-TiO₂ composite) had a little decomposition efficiency, which only removed 20% after UV irradiation for 300 min. For sample CAT3, after irradiation under UV light for 30 min, the concentration of MB solution was reduced 26%, and declined slowly until UV irradiation for 150 min, which only reduced 40%. However, the concentration of MB solution was reduced suddenly from 40% to 80% after irradiation under UV light from 150 min to 300 min. Samples CAT1 and

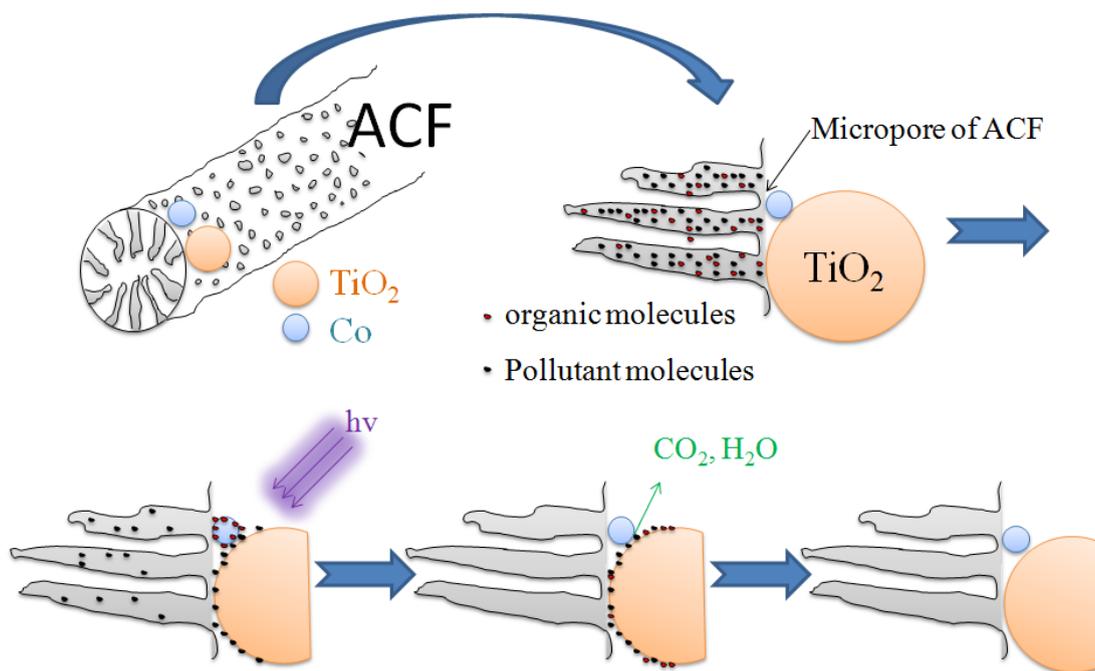
CAT2 was reduced the concentration of MB solution 25% and 41% after UV irradiation for 30 min, respectively. And decompose the MB solution quickly after UV irradiation for 150 min, which almost removed 78% and 87%, respectively. Finally, the decomposition efficiency reached almost 100% under 300 min reaction. It can be considered that at the former 150



[Fig. 4] Dependence of relative concentration of MB in the aqueous solution c/c_0 on time of UV irradiation for the Co-ACFs/TiO₂ composites prepared with TNB and cobalt chloride modified ACFs.

min irradiation time, the samples CAT1 and CAT2 mainly performed the adsorption effect by ACFs, thus the concentration of MB solution reduced quickly. Because the sample CAT3 had most amount of Co element, so the adsorption effect was reduced by Co particles coated on the ACFs surface. However, at the later 150 min irradiation time, the sample CAT3 mainly performed the photocatalytic effect by TiO₂, thus the concentration of MB solution reduced quickly. Because the samples CAT1 and CAT2 had relative fewer amount of Co element, which reduced the electron transition effect by cobalt, thus reduced the photocatalytic effect

As we think, there are 5 essential steps in heterogeneous photocatalysis: (1) reactants reached the surface of catalyst by diffusion; (2) reactants were adsorbed on the surface of catalyst; (3) reactants reacted with catalysts to produce products; (4) products were desorbed from catalysts; (5) products departed the surface of catalyst by diffusion [3]. For the photocatalysis of low concentration



[Fig. 5] Schematic illustration of adsorption, photocatalysis and regeneration of Co-ACFs/TiO₂ catalyst.

organic pollutants, the steps (2) and (4) were control steps by affecting the reaction rate based on the theory of chemical kinetics. Therefore, when TiO₂ catalyst was loaded on supports with high surface area, i.e. ACFs, the organic pollutants were selectively adsorbed on adsorbent supports, resulting in higher pollutant environment around the loaded TiO₂. Then the adsorbed pollutants were transferred to the catalyst by diffusion and then decomposed there at rates, which depend on their adsorption strength [23]. After migration of photocatalytic products from TiO₂ surface. The adsorption and photocatalysis of Co-ACFs/TiO₂ system were regenerated. The synergistic effect of TiO₂ and activated carbon fibers are denoted in Fig. 5.

loaded TiO₂ consisted of mixed crystalline phase of anatase and rutile from the XRD patterns. The EDX spectra show the main peaks of C, O and Ti. Finally, we determined the photocatalytic activity of MB solution for Co-ACF/TiO₂ composites. The Co-ACFs/TiO₂ composites system was efficient especially for the decomposition of organic pollutants in wastewater. The Co-ACFs/TiO₂ photocatalyst developed in this work exhibited obvious photocatalytic reactivity in the degradation of concentrated methylene blue in aqueous solutions, under the dual action of adsorption by ACFs and photocatalytic decomposition by TiO₂. Due to the cobalt has electron transition effect, thus improved the photodegradation of MB solution.

4. Conclusions

TiO₂ catalysts loaded on Co-ACFs support were prepared by sol-gel method. From the SEM images, it is clear that the particles of TiO₂ and the particles of ACFs, and the particles of TiO₂ aggregated into clusters were fixed on the surface of ACFs. Experiment indicated that

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