

Photo Catalytic Activity of CNT-TiO₂ Nano Composite in Degrading Anionic and Cationic Dyes

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Abstract

A CNT-TiO₂ nano composite was prepared from titanium chloride (TiCl₄) via sol-gel process using multi walled carbon nano tube (MWCNT) followed by calcination at 450°C. Spectral analysis revealed that the formed TiO₂ resided on the carbon in anatase form. The effect of adsorption was investigated using aqueous solution of methylene blue and procion blue dye. The photochemical reaction of CNT-TiO₂ composite in aqueous suspensions was studied under UV illumination in batch process. The reaction was investigated by monitoring the discoloration of the dyes employing UV-Visible spectro-photometric technique as a function of irradiation time. The catalyst composites were found to be efficient for the photo-degradation of the dye.

Keywords : Titanium dioxide, Photocatalyst, Carbon nanotubes, Composite

1. Introduction

Titanium dioxide is an inexpensive photocatalyst material using light to degrade environmental pollutants from industrial wastewater owing to its ability to convert them into innocuous end products such as CO₂ [1-3].

Advanced oxidation process using this catalyst appears to be a promising field of study, which has been found to be effective near ambient condition for the degradation of soluble organic contaminants by hydroxyl radical. The usage of UV light and semiconductor photocatalyst TiO₂ can degrade and even mineralize colored dyes [4-7]. Research works were focused on the preparation TiO₂ with carbon composites due to the coupling effect of adsorption and photodegradation [8-11]. Further, presence of carbon prevents the titanium dioxide phase transformation to rutile during heat treatment and can maintain its photoactive anatase phase. It leads to easy mineralization of the concentrated pollutants as well as its intermediate products on the composite material with enhanced activity [12,13].

Carbon particles have been used for the photocatalytic composite with many purposes. Carbon particles work on adsorbent agents, dispersants for avoiding photocatalyst agglomeration and increment of the effective surface area [14,15]. Specially, carbon nanotubes (CNTs) have very high surface-to-volume ratio and unique structures. CNTs are chemically inert at low temperature and are ideal supports in composites. Nano carbon composite materials are using for

interesting applications in many fields due to their unique properties compared to bulk material and have been the subjects of numerous studies [16-18]. The hybridized CNT-TiO₂ nano materials will combine the photocatalytic activity of TiO₂ and high adsorption ability of CNT.

In the present study, nano composite of CNT-TiO₂ was prepared from TiCl₄ and MWCNT by sol-gel method. The degradation of procion blue and methylene blue dyes in aqueous solution was investigated using the prepared CNT-TiO₂ nano composites. The effect of CNT on the optical properties of composite was observed by measuring the degree of photocatalytic degradation of aqueous methylene blue (MB) dye solution and procion blue (PB) dye solution under UV light in batch mode.

2. Experimental

2.1. Chemicals

The methylene blue (C₁₆H₁₈ClN₃S) as cationic dye and procion blue (C₂₉H₁₇ClN₇Na₃O₁₁S₃) as anionic dye were purchased from Acros organics in USA. And the MWCNT (multi walled carbon nanotube) was from Sigma-aldrich in Germany. These CNTs have the properties of above 200 m²/g BET surface area, outer diameter 10~30 nm and inner diameter 3~10 nm. The TiCl₄ (Kanto chemical co., Japan) was used as a precursor of TiO₂. Hydrochloric acid solution

Table 1. Sample Names and Composition of Preparation

Sample name	TiCl ₄	MWCNT	wt% of carbon contents
C0	3.0 ml	-	0
C1	3.0 ml	0.052 g	1
C5	3.0 ml	0.273 g	5

Table 2. Sample Names and Composition (Atomic Percent) of Preparation

Sample name	C (at%)	O (at%)	Ti (at%)
C0	-	69.35	30.65
C1	3.91	71.66	24.43
C5	20.94	57.60	21.46

and ammonia solution were bought from Samchun pure chemical Co. in Korea and Junsei chemical Co. in Japan each. The water employed in the studies was distilled one.

2.2. Preparation of CNT-TiO₂ composite

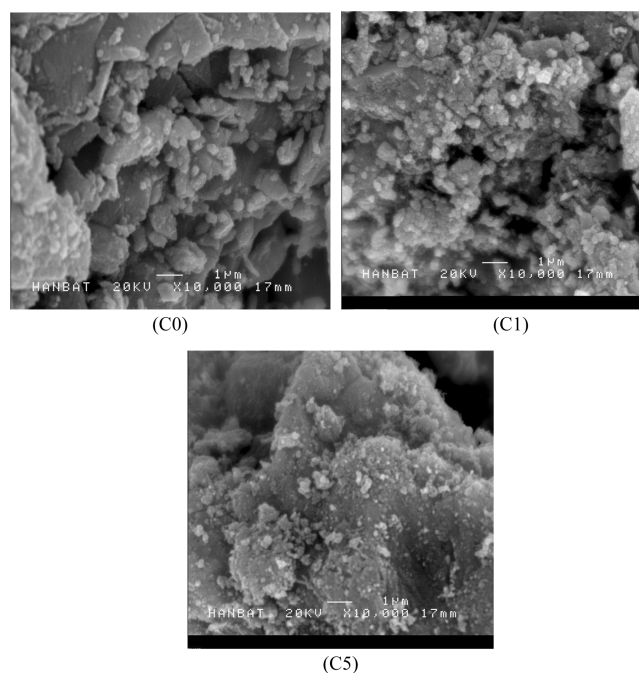
Various amount of multi walled carbon nanotube (MWCNT) was added to 100 ml of 1 M HCl solution and mixed. 3.0 ml of TiCl₄ was added (drop by drop) to the solution. Immediately pH was adjusted to 3 with concentrated ammonia solution. After stirring for 24 h, the sol-gel of Ti(OH)₄ formed with CNTs was washed abundantly with distilled water and heat treated at 350°C for 6 h. The solid was grinded into powder. The Table 1 shows sample names and composite of preparation. The prepared catalyst was characterized by SEM (scanning electron microscope, Jeol Ltd, Japan), XRD (X-ray diffraction, Rigaku International Corporation, D/MAX-2200 Ultima/PC, Japan), and EDS (Energy dispersive X-ray, Horiba, EX-250, Japan).

2.3. Degradation studies

The MB dye solution and PB dye solution of 10 mg/L were prepared by dilution from 1000 mg/L. To 100 ml solution of 10 mg/L of MB and PB in glass beaker, 0.1 g prepared catalyst was added. Samples in the dye solutions were illuminated by UV lamp (Spectroline spectronics Co., USA) of wavelength 365 nm with 4 W. At the first 5 min, 3 ml of examined solution were filtered for measuring the initial adsorption. At regular 15 min intervals of time, 3 ml of the examined solutions were filtered with nylon syringe filter(0.45 μm) to remove suspended impurities. The absorbance of the MB solutions and PB solution was measured using an Optizen UV-visible spectrophotometer at 660 nm and 600 nm each to investigate the degradation efficiency.

3. Results and Discussion

The samples were investigated by SEM in order to study

**Fig. 1.** SEM images of the CNT-TiO₂ composite in this study.

the interaction and composition among the constituents in the CNT-TiO₂ photocatalyst. The SEM images of 10,000 magnifications of the prepared catalysts are shown in Fig. 1 which indicates that the composite materials present a homogeneous distribution of TiO₂ on the CNTs. So it was considered that CNT-TiO₂ composites could have much more activity and show an excellent photocatalytic activity. As the TiO₂ content decreases, the CNTs are seen with aggregates of TiO₂ particles. The observed morphology of composites is desirable for photocatalytic applications.

The results of EDS elemental microanalysis of CNT-TiO₂ composites were manifested in Table 2 and Fig. 2. These showed the presence of C, O and Ti and demonstrated the influence of mix ratio. The expected C content increased with the increasing dosing CNT amount while the content of Ti and O decreases in the composites. It means the TiO₂ ratio decreased with increasing dosing CNT amount.

The XRD patterns of the CNT-TiO₂ composites were displayed in Fig. 3. The patterns demonstrate the highly crystalline nature of the composites. The peaks at 25.3, 37.8, 48.0, 54.9 and 62.5 were the diffractions of (101), (004), (200), (211) and (204) planes of anatase, respectively, which indicating the developed CNT-TiO₂ composites existed in anatase state. This also indicates that the precursor, TiCl₄ was converted to anatase TiO₂ via amorphous Ti(OH)₄ upon heating at 350°C and the prepared anatase TiO₂ deposited on the MWCNTs under the experimental conditions. This clearly indicates that heat treatment at this temperature is sufficient, since high temperature may lead to poorly photoactive rutile form. Enache et al. also recommended this

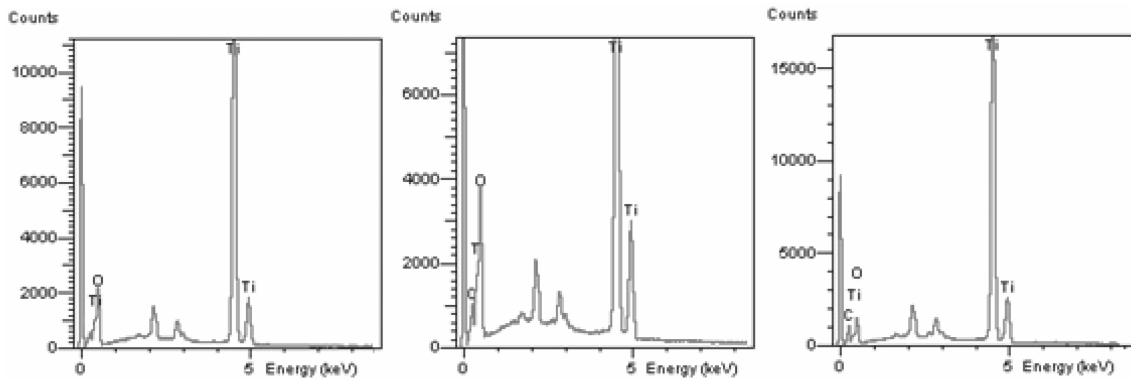


Fig. 2. The results of EDS elemental microanalysis of CNT-TiO₂ composites.

temperature as effective one to get highly photoactive anatase crystalline form [19].

The negligible photocatalytic activity of amorphous TiO₂ is attributable to the facilitated recombination of photo-excited electrons and holes in the amorphous structure. Therefore, the result in Fig. 3 suggests that TiO₂ synthesized by TiCl₄ has structure with high crystallinity that prevents the electron-hole recombination.

The photocatalytic activity of the CNT-TiO₂ composite in the degrading dyes was examined under UV illumination. Fig. 4 and Fig. 5 show the degradation results of the dye solution using naked TiO₂ and CNT-TiO₂ composite which made from different mixing ratio of TiCl₄ and CNT according to UV illumination time. The adsorption efficiency of the dyes on the catalyst surface was observed in initial rapid decrement of the dye concentration. And Photocatalytic activity may be observed from slope of dye concentration.

When UV illumination was carried out to the reactor, photo-degradation of dye occurred by TiO₂, adsorption of dye mainly occurred by CNT. From these results, the prepared catalysts show the high photocatalytic activity and adsorption at the removal of MB and PB. The increment of

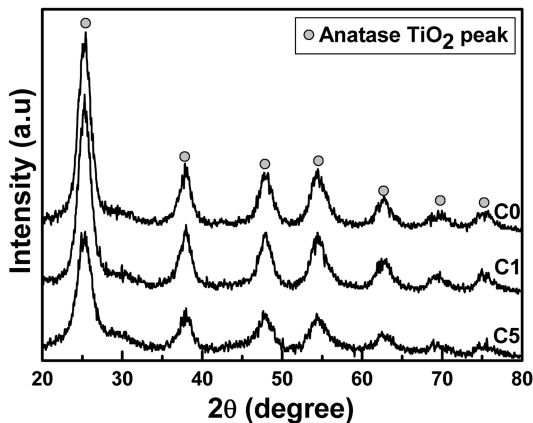


Fig. 3. The XRD patterns of the CNT-TiO₂ composites.

CNT mixing ratio in the composite leads the increased photocatalytic activity and adsorption ability. This is due to the

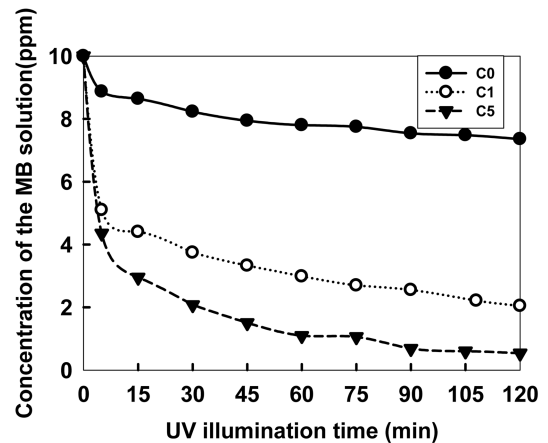


Fig. 4. Degradation results of the MB solution with the photocatalysts which made from different mixing ratio of TiCl₄ and CNT according to UV illumination time.

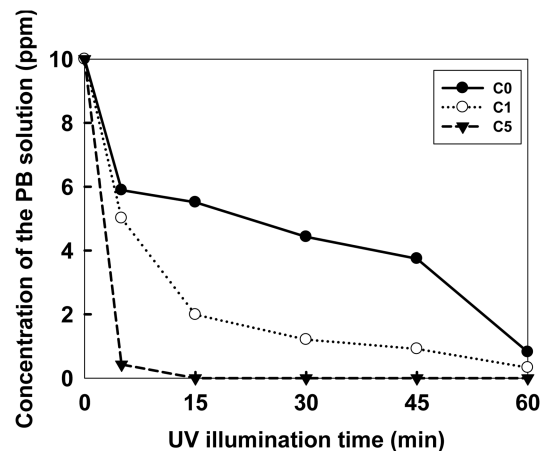
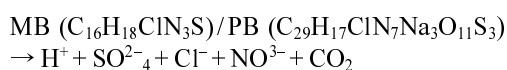


Fig. 5. Degradation results of the PB solution with the photocatalysts which made from different mixing ratio of TiCl₄ and CNT according to UV illumination time.

increment of CNT coverage on the surface according to the increment of dosing CNT. During initial 5 minutes, the dyes were rapidly removed in all case due to the synergetic effect of the solid nano materials. But, after 15 minutes, adsorption does not continue due to the adsorption capacity limit.

The photodegradation ability of the samples also improved with the increment of dosing CNT. This indicates that the interaction of TiO₂ particles and MWCNTs may modify the process of the electron/hole pair formation under UV light irradiation [20]. So it may be the unique structure of the CNT-TiO₂ composites that led to the high catalytic activity. Furthermore, because the band gap of C is smaller than that of TiO₂, it can be excited easily under irradiation of UV light. MWCNTs are induced to generate electron (e^-) by UV light irradiation, and the photo-induced electrons transferred to the conduction band of TiO₂ and electrons of valance band (VB) of TiO₂ transferred to MWCNTs simultaneously. In other word, the positive charged holes (h^+) formed while the induced electrons migrated from MWCNTs to TiO₂. The injecting electrons from MWCNTs to TiO₂ could catch the O₂ adsorbed on the surface of TiO₂ to yield very active radicals, superoxide radical ions, and the positive charged hole could catch OH⁻ to yield hydroxyl radicals. Both superoxide radical ions and hydroxyl radicals were responsible for the photoactivity.



4. Conclusions

CNT-TiO₂ composites were prepared by sol-gel method successfully. The SEM images revealed that the CNT was covered with TiO₂ particles in all the samples. Photocatalytic activity and adsorption was increased with increasing the ratio of CNT of composite in the dye solutions. During the first 5 min, CNT-TiO₂ composites mainly adsorb dye solution but after 15 min, it mainly showed the photodegradation. TiO₂-CNT samples have the continuous degradation ability under the UV illumination and the dye removal of TiO₂-CNT composites was better than that of pristine TiO₂.

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