Enhancement of Photocatalytic Decolorization of Methylene Blue Over WO₃/CNT Incorporated TiO₂ Nanocatalysts Under UV Light Radiation

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The photodegradation of methylene blue solution catalyzed by anatase TiO₂ and composite photocatalysts: WO₃/TiO₂, WO₃/CNT/TiO₂ (with different content of W) was studied under irradiation with UV light. The catalysts were characterized by SEM, TEM, BET, XRD, EDX and UV-VIS absorption spectroscopy. The results showed that MWCNTs used as supports materials efficiently inhibit the agglomeration of WO₃/TiO₂ and improve the dispersion of nanoparticles. The photoactivity of the prepared materials under UV irradiation was tested using the conversion of methylene blue in aqueous solution. In comparison with non-nanocarbon supported WO₃/TiO₂ composites, the nanocarbon supported WO₃/TiO₂ composites had higher absorption ability with a larger specific surface area and showed higher photocatalytic activity of degradation methylene blue solution under UV light irradiation, meanwhile it was found that an optimal WO₃ dosage of 8.80 wt % in WO₃/CNT/TiO₂ composite achieved the highest photodegradation rate in this study. It can be considered that the methylene blue removal effect of the WO₃/CNT/TiO₂ composite is affected by two kinds of effects: adsorption effect by MWCNTs and photocatalytic effect by TiO₂. Finally, the reasons for the obvious increase of photocatalytic activity indicated that the effect of MWCNTs, which could absorb UV light to create photoinduced electrons (e⁻) and the electron trapping effect of WO₃, which resulted in the recombination rate of electrons/holes in WO₃/CNT/TiO₂ declined.

Key Words: Tungsten oxide/MWCNTs, Titanium dioxide, Photocatalytic properties, UV light, Methylene blue.

INTRODUCTION

At present energy and environmental crisis is the very serious challenge of survival and development for modern humans. Environmental protection has attracted more and more attention through various approaches. Photocatalytic purification of water and air has been considered as one of the promising methods. Among many of the photocatalyst, TiO₂ is widely used as a most excellent photocatalyst due to its semiconductor characteristic, high photocatalytic activity, strong oxidation ability, low energy consumption, low cost, chemical stability and non-toxicity.

However, the use of TiO₂ as photocatalysts is limited mainly to the recombination of the generated photo-holes and photo-electrons. Photocatalysis involves the oxidation of a chemical by photo-holes from the semiconductor, so every recombination event involves the loss of holes that might otherwise have promoted degradation. Therefore, the major transfer of photogenerated electrons and holes between the valence and conduction bands of semiconductors is important to photocatalysis. Various methods have been reported to

improve photocatalytic efficiency by the modification of surface or bulk properties, *i.e.*, doping, codeposition of metals, surface chelating, mixing of two semiconductors, coating of an insulating oxide layer, *etc.*¹⁻⁵.

The mechanism of coupled semiconductors is to increase the photocatalytic efficiency by increasing the charge separation and extending the photo-responding range. Now, the research about doping another semiconductor on the surface of TiO₂ includes SnO₂-TiO₂^{6,7}, V₂O₅-TiO₂⁸, ZnO-TiO₂⁹, ZrO₂-TiO₂^{10,11}, CdS-TiO₂¹². Since WO₃ has a slightly lower conduction band than TiO₂, the photoelectrons are prone to transfer from the conduction band of TiO₂ to that of WO₃ and result in the effective charge carrier separation when TiO₂ nanotube array is coupled with WO₃¹³⁻¹⁵. It has been reported that TiO₂ nanotube arrays coupled with WO₃ possess enhanced electrochromic properties and a significantly lower threshold voltage¹⁶. Do *et al.*¹⁷ found the degradation rate of 1,4-dichlorobenzene was enhanced by addition of WO₃ on the surface of TiO₂.

However, as other powder photocatalysts, WO₃/TiO₂ nanoparticles have some disadvantages, such as difficult recovery, easy cohesion and low utilization rate in practical

applications. Some alternative methods are immobilizing nanoparticles onto an inert and porous supporting matrix; through the accumulation of carriers the adsorption mass transfer rate and efficiency of photocatalytic degradation are effectively improved¹⁸⁻²¹. As a good support for nanomaterials, multi-walled carbon nanotubes (MWCNTs) efforts have been made to explore their applications using various approaches since the discovery by Iijima²², as they are in fact one of the most remarkable emergent materials. In a recent review, attention has been drawn to the fact that CNT can compete with activated carbon as catalyst supports and peculiar behaviours in terms of conversion or selectivity, which were attributed to the combination of their electronic, specific active-phase-support interaction, adsorption, mechanical and thermal properties²³.

Because of their great hardness and toughness, CNT maintain their morphology and structure even at high nanoparticle loadings. In past, a variety of metal oxides, such as GeO_2 , Eu_2O_3 , V_2O_5 , ZnO , RuO_2 , *etc.*, have been decorated to the surface of CNTs by some research groups²⁴⁻²⁸. The combination of CNTs with metal oxide nanoparticles can be used as catalysts, sensors, semiconductor devices, data storage/processing devices and new reinforced nanofiber materials²⁹.

In consideration of the basic disadvantage of WO_3 as a photocatalyst which has a low photonic efficiency. In this report, we combined both advantage of introducing MWCNT and WO_3 , successfully fabricated a novel photocatalyst through the method of sol-gel-dipping-calcination with the aim of: (i) determine the decolorization efficiency of methylene blue at various reaction times for different samples; (ii) elucidate the effects of WO_3 on decolorization efficiency; (iii) enhance the step of the application of the technology of nano particulate TiO_2 photodegradation and improving the particle size distribution structure; (iv) establish the convenient dye-photodegradation mechanisms using $\text{WO}_3/\text{CNT}/\text{TiO}_2$ composites.

EXPERIMENTAL

The ammonium metatungstate hydrate ($\text{H}_{26}\text{N}_6\text{O}_{40}\text{W}_{12}\cdot x\text{H}_2\text{O}$) purchased from Sigma-AldrichTM Chemie GmbH (Germany) was used as raw material to decomposition generate WO_3 at high temperature. The titanium(IV) *n*-butoxide (TNB, $\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$) as a titanium source for the preparation of the $\text{WO}_3/\text{CNT}/\text{TiO}_2$ composites was purchased as reagent-grade from Acros Organics (USA). MWCNTs (95.5 %) powder with diameter of 20 nm and length of 5 μm was purchased from Carbon Nano-material Technology Co. Ltd., Korea. For the oxidization the surface of MWCNTs, MCPBA (*m*-chloroperbenzoic acid) was used as an oxidizing reagent purchased from Acros Organics, New Jersey, USA. Benzene (99.5 %) and ethyl alcohol were purchased as reagent-grade from Duksan Pure Chemical Co. (Korea) and Daejung Chemical Co. (Korea) and used without further purification unless otherwise stated. Methylene blue ($\text{C}_{16}\text{H}_{18}\text{N}_3\text{SCl}\cdot 3\text{H}_2\text{O}$) was analytical grade and also purchased from Duksan Pure Chemical Co. Ltd. (Korea).

Synthesis of $\text{WO}_3/\text{CNT}/\text{TiO}_2$ photocatalyst: For designing an effective photocatalyst ($\text{WO}_3/\text{CNT}/\text{TiO}_2$), we used a new synthesize process. As is well-known, the MWCNT is so stable that it needs to be treated with strong acids to introduce active

function groups on their surface for many applications. Thus 2 g of *m*-chloroperbenzoic acid was dissolved in 80 mL benzene and then 1 g CNT powder was put into the oxidizing agent solution, refluxed at 353 K for 6 h then the solid precipitates were formed and dried at 363 K. Then the treated MWCNTs were milled and washed with distilled water and ethanol and dried at 333 K in vacuum.

In order to synthesize three kinds of WO_3/CNT compounds, different contents of $\text{H}_{26}\text{N}_6\text{O}_{40}\text{W}_{12}\cdot x\text{H}_2\text{O}$ powder was added to 60 mL of water in three breakers, respectively and stirred until they were completely dissolved. Further 0.3 g of oxidized CNT was taken out and added to this mixture separately and stirred magnetically at 353 K. After reaction for 10 h, the formed gels were refluxed at 373 K for 8 h and then heat treatment at 773 K for 1 h with a heating rate of 279 K/min. Finally, three kinds of WO_3/CNT composites were obtained and named WC1, WC2, WC3.

On the other hand, 4 mL of titanium *n*-butoxide was dissolved in 80mL of benzene to get the sol. The WC1, WC2, WC3 composites was put into the sol, after homogenized at 353 K for 8 h using a shaking water bath (Lab house, Korea) with a shaking rate of 120 rpm/min, the $\text{WO}_3/\text{CNT}/\text{TiO}_2$ gels were obtained. The $\text{WO}_3/\text{CNT}/\text{TiO}_2$ gels were heat treated at 773 K for 1 h to form the $\text{WO}_3/\text{CNT}/\text{TiO}_2$ photocatalysts which named WCT 1, WCT 2, WCT 3. The procedure of prepared samples is shown in Fig. 1. The preparation conditions and the sample code used in this study were listed in Table-1.

Fig. 1. Preparatory procedure of WO_3/TiO_2 and $\text{WO}_3/\text{CNT}/\text{TiO}_2$ composite

TABLE-1
NOMENCLATURES OF SAMPLES PREPARED WITH
 WO_3/TiO_2 AND $\text{WO}_3/\text{CNT}/\text{TiO}_2$ COMPOSITE

Preparation method	Nomenclatures
$\text{H}_{26}\text{N}_6\text{O}_{40}\text{W}_{12}\cdot x\text{H}_2\text{O}$ + benzene + TNB	WT
Oxidized CNT + $\text{H}_{26}\text{N}_6\text{O}_{40}\text{W}_{12}\cdot x\text{H}_2\text{O}$ 1 + 2 mL TNB	WCT1
Oxidized CNT + $\text{H}_{26}\text{N}_6\text{O}_{40}\text{W}_{12}\cdot x\text{H}_2\text{O}$ 2 + 2 mL TNB	WCT2
Oxidized CNT + $\text{H}_{26}\text{N}_6\text{O}_{40}\text{W}_{12}\cdot x\text{H}_2\text{O}$ 3 + 2 mL TNB	WCT3

TNB = Titanium *n*-butoxide

For comparison and verification the photocatalytic effect of WO_3/TiO_2 , the composite was performed by titanium *n*-butoxide as TiO_2 source with a solution of $\text{H}_{26}\text{N}_6\text{O}_{40}\text{W}_{12}\cdot x\text{H}_2\text{O}$ by a sol-gel method. Some amount of $\text{H}_{26}\text{N}_6\text{O}_{40}\text{W}_{12}\cdot x\text{H}_2\text{O}$

powder dissolved in very little amount of distilled water and 50 mL of benzene was added to it under continuous stirring. Further 4 mL TNB was added to the solvent under magnetic stirring for 8 h at 353 K. The obtained mixture was dried at 373 K for 5 h and calcined at 773 K for 1 h.

Characterization of catalysts: SEM (scanning electron microscopy, JSM-5200 JOEL, Japan) was used to observe the morphology and microstructure of WO₃ modified TiO₂ and the samples of MWCNTs introduced WO₃/CNT/TiO₂ composites with increased content of W.

Transmission electron microscopy (TEM, JEOL, JEM-2010, Japan) at an acceleration voltage of 200 kV was used to investigate the size and distribution of the WO₃ and TiO₂ deposits on the MWCNTs surface of various samples. TEM specimens were prepared by placing a few drops of the sample solution on a carbon grid.

For the determination of the crystallographic structure of the inorganic constituent of the composites, X-ray diffraction analysis (XRD) was taken using an X-ray generator (Shimadzu XD-D1, Japan) with CuK α irradiation (0.154056 nm) at room temperature. The nature of the phase in the sample was checked using the database of the Joint Committee on Powder Diffraction Standards (JCPDS).

EDX spectra were also used for the elemental analysis of the samples. The Brunauer-Emett-Teller (BET) surface area of these photocatalyst composite was determined by N₂ adsorption measured at 77 K using a BET analyzer (Monosorb, USA). For the analysis of photo-degradation effects, UV-VIS adsorption parameters for the WT, WCT1, WCT 2, WCT 3 composites were recorded by a UV-VIS (Optizen Pop Mecasys Co., Ltd., Korean) spectrophotometer.

Determination of photocatalytic properties: Photocatalytic activities were evaluated by methylene blue degradation in aqueous medium at ambient temperature under ultraviolet light irradiation with a wavelength of 365 nm and 20 W output. The UV lamp was used at the distance of 100 mm from the solution in darkness box. The initial methylene blue concentration (c_0) was 1.0×10^{-5} mol/L. And the amount of photocatalyst composites was kept at 10 mg. Before turning on illumination, the suspension solution containing 50 mL of methylene blue and the photocatalyst composites was placed for 2 h in the darkness box to establish an adsorption-desorption equilibrium. Experiments were then carried out under UV light. Solution was withdrawn regularly from the reactor by an order of 30, 60, 90 and 120 min and immediately centrifuged to separate any suspended solid. The clean transparent solution was analyzed by using a UV-VIS spectrophotometer. Then, the full spectrum (200-750 nm) of each sample was recorded and the characteristic absorption of methylene blue at 665 nm was chosen as the monitored parameter for the photocatalytic degradation process.

RESULTS AND DISCUSSION

SEM and TEM analysis: The typical micro-surface structures and morphology of the WT and WCT composites were characterized by SEM (Fig. 2) and TEM (Fig. 3). Fig. 2 shows the macroscopical changes in the morphology of WT and WCT. As shown in Fig. 2(a), TiO₂ and WO₃ were agglomerated with

(a)

(b)

(c)

(d)

Fig. 2. SEM micrographs of WO₃/TiO₂ and WO₃/CNT/TiO₂ composites: (a) WT, (b) WCT1, (c) WCT2, (d) WCT3

(a)

Fig. 3. TEM micrographs of $\text{WO}_3/\text{CNT}/\text{TiO}_2$ composite: (a) WCT1, (b) WCT3

each other thus we could not find the exact crystal morphology, it can be attributed that when the crystal particle size is very small, it can easily agglomerate due to the weak forces of the surface. From Fig. 2(b-d), the porous structure can be observed and the TiO_2 agglomerate is coated on the WO_3/CNT composite. However, small amounts of TiO_2 particles were also aggregated to be bundles, which possibly are not well homogenized during vigorous stirring. It was considered that better dispersion enables larger number of active catalytic centers for the photocatalytic reaction³⁰. These results are also confirmed by TEM inspection of the $\text{WO}_3/\text{CNT}/\text{TiO}_2$ composite. As shown in Fig. 3, for the $\text{WO}_3/\text{CNT}/\text{TiO}_2$ composite, the TiO_2 particles were distributed uniformly outside surface of CNT tube, WO_3 particles were completely attached on the surface of the tube this caused partial agglomeration to form blocky-shaped particle. Most of the WO_3 was in the quasi-spherical shape, *ca.* 5-15 nm in size, coating the outside surface of the MWCNT, very few isolated WO_3 particles were observed. The average size of the TiO_2 particles was smaller than that of the WO_3 particles. Therefore, the higher photocatalytic activity of the $\text{WO}_3/\text{CNT}/\text{TiO}_2$ composite might be attributed to the small and nano-sized distribution of titanium complexes including titanium dioxide, the energy sensitizer for improving the quantum efficiency and an increase of charge transfer of the MWCNTs.

BET surface area analysis: The values of the BET surface area of CNT, WT, WCT 1, WCT 2, WCT 3 samples are presented in Table-2. The BET surface area of CNT and WO_3/TiO_2 were 211.43 and 38.44 m^2/g . The BET surface areas of WCT 1, WCT 2, WCT 3 were 93.64, 101.43 and 99.13 m^2/g , respectively. It is clearly shown that the agglomeration is caused easily in the process of WO_3/TiO_2 preparation because of its higher surface energy. When CNT was introduced in WO_3/TiO_2 composite, it can prevent TiO_2 particles and WO_3 particles form agglomerating, thus there was large change of the micro-pore size distribution for $\text{WO}_3/\text{CNT}/\text{TiO}_2$ composite compared to that of corresponding WO_3/TiO_2 . This indicated that the supported CNT was directly related to adsorption ability of TiO_2 .

TABLE-2
BET SURFACE AREA OF $\text{WO}_3/\text{CNT}/\text{TiO}_2$ COMPOSITE

Samples	S_{BET} (m^2/g)
Original MWCNT	211.43
WT	38.44
WCT1	93.64
WCT2	101.43
WCT3	99.13

XRD analysis: The XRD analysis results for the catalysts are shown in Fig. 4. Diffraction peaks corresponding to anatase are marked with 'A'; diffraction peaks corresponding to the WO_3 phase are marked with 'W'. In the XRD patterns for the carbon nanotube non-treated WT composite, the diffraction peaks of tungsten oxide were certainly observed because of the high tungsten content and high crystallinity. The sharp peaks corresponding to 23.2, 24.5, 28.3, 34.1 and 36.8° 2 θ were indicative of monoclinic WO_3 ³¹ increasing with the W content. For the WCT composites, the major peaks at 25.3, 37.8, 48.0, 53.8, 54.9 and 62.5° 2 θ were assigned to diffraction planes of (101), (004), (200), (105), (211) and (204) of anatase, indicating the prepared WCT composite existed as anatase. One broad peaks are measured at 2 θ values of approximately 25.80°. It's the characteristic peaks corresponding to the MWCNTs molecular crystal structure. These peaks correspond to d-values of 0.345 nm³². MWCNTs and one of titanium characteristic peaks are overlap at around 25.0°, so intensity of the peak is increased.

Fig. 4. XRD analysis of WO_3/TiO_2 and $\text{WO}_3/\text{CNT}/\text{TiO}_2$ composite

EDX analysis: The quantitative microanalysis of C, O, Ti and W as major elements for the WO_3/TiO_2 and $\text{WO}_3/\text{CNT}/\text{TiO}_2$ composites was performed by EDX. The EDX spectra of the WO_3/TiO_2 and $\text{WO}_3/\text{CNT}/\text{TiO}_2$ composites are shown in Fig. 5. The results of the EDX elemental microanalysis of the WO_3/TiO_2 and $\text{WO}_3/\text{CNT}/\text{TiO}_2$ composites were listed in Table-3. From the EDX data, the main elements such as C, O, Ti and W existed. The contents of the tungsten component for WT, WCT 1, WCT 2 and WCT 3 are 61.57, 5.48, 8.8 and 11.15 %, respectively. It can be expected that the contents of the tungsten component in the composites increased with an increase of WO_3 concentrations. In case of most of the samples, carbon and titanium were present as major elements with small quantities of oxygen in the composite.

TABLE-3
EDX ELEMENTAL MICROANALYSIS OF
 WO_3/TiO_2 AND $\text{WO}_3/\text{CNT}/\text{TiO}_2$ COMPOSITE

Samples	Elements (wt %)			
	C	O	Ti	W
WT	0	26.51	11.92	61.57
WCT1	33.95	28.49	32.08	5.48
WCT2	37.21	22.86	31.13	8.80
WCT3	28.59	28.10	32.17	11.15

Fig. 5. EDX analysis of WO₃/TiO₂ and WO₃/CNT/TiO₂ composite: (a) WT, (b) WCT1, (c) WCT2, (d) WCT3

Photocatalytic degradation of methylene blue: The adsorption abilities and photodegradation efficiency of pure TiO₂, WT, WCT 1, WCT 2 and WCT 3 composites evaluated with 2 h placed in the dark box and excited UV light were shown in Fig. 6. It was quite easy to draw a causal relationship between surface areas in Table-2. It was clear that adsorption abilities of methylene blue on WCT samples were faster than that of pure TiO₂ powder. This was attributed to the high porosity of the WCT surface due to introduction of porous carbon material- MWCNTs, which correlated with an increase in adsorption ability.

In Fig. 6 it also shown that for degradation of methylene blue solution the photocatalytic activity of WT was higher than that of the pure TiO₂ but the WCT photocatalyst exhibited an excellent photocatalytic activity of three kinds of samples. However, for WCT 1, WCT 2 and WCT 3 these three kinds of photocatalyst, with increasing the content of W, the photocatalytic efficiency was not correspond to the increase. The WCT 2 sample with W content of 8.80 % shown the best photocatalytic decolorization ability of methylene blue solution, it can be considered that using a larger amount of WO₃

Fig. 6. Removal of the methylene blue solution by pure TiO₂, WO₃/TiO₂, WO₃/CNT/TiO₂ composites

as dopant, on the contrary the WO₃ was easy to be the recombination center of electron-hole pairs which results that decrease the photocatalytic efficiency.

As mentioned above, to increase the efficiency of the photodegradation of dye, we may increase the amount of electron (e^-) and prevent the recombination of the electron-hole. As studies, MWCNTs had an energy sensitizer for improving the quantum efficiency and an increase of charge transfer. It is believed that the high efficiency degradation of methylene blue concentration in the aqueous solution can be occurred in three physical phenomena such as from the quantum efficiency of the MWCNTs, photogenerated electrons trap effect of WO₃ and photocatalytic decomposition by TiO₂. methylene blue molecules absorb energy from irradiation, thereby shifting their delocalized electrons from bonding to antibonding orbitals. Since methylene blue adsorption likely occurs *via* π - π interactions between its delocalized electrons and the graphene layers of carbon, it is reasonable that shifts in its electron orbitals would alter adsorption. It is considered that the TiO₂ deposited on the MWCNTs surface can retain its photo-degradation activity.

The tungsten oxide dopant in the titania crystalline matrix can prevent the recombination which promotes the efficiency of TiO₂. Furthermore, when the WO₃/CNT/TiO₂ composite was irradiated with UV light, according to some studies under UV light irradiation, the MWCNT can absorb UV light to create photo-induced electrons (e^-) into the conduction band (CB) of the TiO₂ particles with increasing amount of electrons^{33,34}. And the essence of the charge separation mechanism in the WO₃-TiO₂ composite consists in electron transfer from the conduction band of TiO₂ to WO₃ conduction band, accompanied by consecutive W^{6+} reduction into W^{5+} , occurring on the surface of the WO₃ crystal lattice³⁵. The electron transfer from the photoactive TiO₂ to WO₃ leads to an increase in the lifetime of the photogenerated pairs and as a consequence to a promotion of the photonic efficiency of the photocatalytic degradation of organic substrates. On the other hand, the photogenerated holes remain on the WO₃ particles and TiO₂ particles theoretically migrate to the surface and react with OH⁻ or H₂O to generate OH[•] and the electrons trapped on WO₃ can react with molecular O₂ to form O₂^{•-} radicals, which

eventually oxidize methylene blue, the reactions can be expressed as follows:

And the reaction mechanism of the $\text{WO}_3/\text{CNT}/\text{TiO}_2$ composite under UV light irradiation was shown in Fig. 7.

Fig. 7. Schematic diagram of the mechanism of preparation and photocatalytic activity of the $\text{WO}_3/\text{CNT}/\text{TiO}_2$ composite

Conclusion

The new photocatalyst composites of $\text{WO}_3/\text{CNT}/\text{TiO}_2$ was prepared by the sol-gel method and its chemical composition and optical absorption were examined by SEM, TEM, XRD, BET and UV-VIS adsorption spectra. The surface area of all the composites is less than that of pristine MWCNTs and compared with WO_3/TiO_2 the surface area was increased after introduction of MWCNTs. According to the TEM images, TiO_2 particles are uniformly dispersed on the surface of MWCNTs with several WO_3 particles between them in case of $\text{WO}_3/\text{CNT}/\text{TiO}_2$ composites. And the size of TiO_2 and WO_3 particles is about 5-15 nm. Finally, the photoactivity of the prepared materials, under UV irradiation, was tested using the conversion of methylene blue from model aqueous solution. The higher efficiency of photo-decolorization of the substrate catalyzed by $\text{WO}_3/\text{CNT}/\text{TiO}_2$ in comparison to anatase TiO_2 can be attributed to the more efficient separation of surface charge carriers in the WO_3/TiO_2 photocatalyst and to an increase in the quantity of generated $\text{HO}^{\bullet}$ radicals on the valence bands of WO_3 and TiO_2 , comprised by the composite photocatalyst as a result of the better adsorption of H_2O and $\text{HO}^{\bullet}$ on its surface. On the other hand, the higher activity of photocatalytic destruction of methylene blue in the case of nanosized MWCNTs as support material coated with WO_3 and TiO_2 particles is owing to increase in the lifetime of the charge carriers and enhancement of the efficiency of the interfacial charge transfer to adsorbed substrates. Especially efficient is the charge separation in the case of the $\text{WO}_3/\text{CNT}/\text{TiO}_2$ photocatalyst during irradiation with UV light, when the optimal WO_3 dosage was 8.80 wt % its photo-decolorization efficiency was higher than that of the process catalyzed by WO_3/TiO_2 and achieved the highest photodegradation rate in this study.

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