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Synthesis and Characterization of $TiO_2/CuO/WO_3$ Ternary Composite and its Application as Photocatalyst

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ABSTRACT

Photocatalytic removal of water and air pollution has received much attention today. Many photocatalysts based on semiconductors have been developed and used. Binary and even ternary composites have been developed to solve the drawback of semiconductors, including high band gaps and short life time of charge carriers. In this study, a three-component composite of $TiO_2/CuO/WO_3$ was synthesized by adding WO_3 to TiO_2/CuO. Their structural properties were evaluated by analyzes X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), and diffusive reflectance spectra (DRS) and their performance by methylene orange dye removal. The results of XRD and SEM analysis showed purity and uniform distribution of elements. The combination of TiO_2/10%CuO and 15%WO_3 with band gap 2.66 eV showed the highest rate constant of dye removal (0.0301 min^{-1}).

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1. INTRODUCTION

Due to the increasing demand for solar energy, treated water and air, and the removal of hazardous and toxic pollutants, the use of semiconductor photocatalysts that have a wide variety of capabilities in these fields have attracted considerable attention [1-4]. Especially TiO_2, which due to its good photocatalytic activity in the removal of organic pollutants such as rhodamine B [5], tetracycline [6], phenols [7], dye reagents [8], etc., has been further studied under ultraviolet irradiation.

Heterogeneous photocatalysts based on advanced oxidation processes using semiconductor materials such as TiO_2 have been of great interest over the past two decades for the treatment of environmental pollution in water and air. However, this technique can not significantly improve the practical quality of water [9]. Because TiO_2 has drawbacks such as: rapid recombination of photo-excited charge carriers (electron-hole) and extensive band gaps [10-14]. The excited direction of TiO_2 in practical applications, due to its low efficiency in photon utilization and relatively high band gap energy (3.0-3.2 eV), requires a source of ultraviolet light illustration, which is only a small part of sunlight (3-5%) [15].

Many strategies have been used to solve these problems to develop the TiO_2 photocatalytic system with improved activity under UV-vis irradiation. Some of these strategies include: use of transition metal ions, precious metal deposition, dye sensitized TiO_2 and coupling with other semiconductors such as ZnO, CdS and WO_3 [16, 17]. Among semiconductors, WO_3 and CuO coupling have been extensively studied. WO_3 with band gap energy of 2.5-2.9 eV improves the photocatalytic efficiency of TiO_2 in various ways. It prevents the recombination of e_{cb}^-/h_{vb}^+ pairs and transmits the useful region of the excitation beam to the visible spectrum [14, 16]. In addition, the presence of WO_3 increases the surface acidity on TiO_2 particles [18]. They are composed in different ways to adsorb more OH^- or H_2O molecules and produce larger amounts of HO° radicals [11, 19]. Accordingly, many studies have evaluated the photocatalytic activity of WO_3/TiO_2 to reduce the amount of methylene blue and methyl orange using light irradiation [16, 20].

Another TiO_2 composite, as a successful combination of monoxide properties, is the CuO/TiO_2 composite,

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which is particularly attractive due to its low p-CuO band gap and high n-TiO_2 reactivity [21, 22]. The p-n junction coupling is expected to produce an improved lifetime of the charge carriers with positive effects on photocatalytic activity [23, 24]. The high photocatalytic activity of CuO/TiO_2 has been attributed to the transfer of photo-excited electrons from the TiO_2 conduction band to the CuO conduction band. This accumulation of extra electrons in the CuO conduction band causes a negative shift in Fermi level and thus improves its photocatalytic performance in removing organic pollutants from water as well as hydrogen production from water [25].

Recently, a number of composites with three compounds have been fabricated and their photocatalytic performance has been investigated. Miwa et al. [26] synthesized $CuO/Al_2O_3/TiO_2$ composite by mechanical method. They showed that the combination of 0.2wt% CuO/0.3wt% Al_2O_3/TiO_2 had a better performance in the photocatalytic production of hydrogen. Yanyan et al. [27] synthesized the $WO_3/TiO_2/SiO_2$ composite by sol-gel method. The results of photocatalytic performance in photodegradation of Ace showed that 3% $WO_3/TiO_2/SiO_2$ had the highest efficiency of 88%. Li et al. [28] showed that the simultaneous addition of 15% MoS_2/MoO_3 to TiO_2 produced a fast degradation rate (maximum ~0.138 min^{-1}), of rhodamine B degradation (95%) in 20 min under visible-light irradiation.

Because in the three compounds due to the difference in the edge of the conduction band and the valence band, after the production of photo-excited charge carriers, electrons and holes are transferred at the junction of these semiconductors, the timelife of the charge carriers increases and the chance their participation in oxidation reactions increases. Therefore, in this work, $WO_3/TiO_2/CuO$ ternary nanocomposites are synthesized. The samples were examined by X-ray diffraction (XRD), Field-emission scanning electron microscopy (FESEM) and diffusive reflectance spectra (DRS) analyzes. To study the photocatalytic performance of synthesized composites, methyl orange removal test is performed.

2. MATERIALS AND EXPERIMENTS

2. 1. Materials In this research, Titanium tetraisopropoxide (TTIP) from Daejung (Korea), hydrochloric acid (HCl), 2-propanol, methyl orange (MeO), WO_3 nanopowder, ascorbic acid and Cupric sulfate pentahydrate ($CuSO_4.5H_2O$) from Merck (Darmstadt, Germany) were purchased.

2. 2. Synthesis of TiO_2-based Composites To make the ternary nanocomposite of $TiO_2/CuO/WO_3$, initially similar to the flowchart of Figure 1 and by adjusting the time and amount of each compound, two solutions were prepared as follows:

Solution A: 6 ml of 2-propanol was mixed with 6 ml of hydrochloric acid and 85 ml of distilled water for 10 min. Then 6 ml of TTIP was added dropwise into the solution and the temperature was slowly raised to 50 °C. The solution was stirred for 60 min.

Solution B: 0.4 g of copper sulfate was dissolved in 100 ml of distilled water and stirred for 20 min. 30 ml of sodium hydroxide 0.05 M was added to the solution. After stirring for 30 min, 30 ml of ascorbic acid 0.05 M was added and stirred for 30 min.

To prepare a ternary composite with a specific composition, certain ratio of solution B were added dropwise into solution A (to achieve a TiO_2 to CuO ratio of 1:9). Also, a certain amount of WO_3 nanoparticle powder was added to it. The resulting solution was stirred for 1 h and then allowed to precipitate for 24 h. The precipitate was calcined after drying for 2 h at 400 °C. The resulting samples were named 5WTC, 10WTC, 15WTC and 20WTC according to the composition of $90TiO_2$-10CuO and the amount of WO_3 at 5, 10, 15 and 20%.

2. 3. Characterizations In order to investigate the phases formed in the composite samples, the XRD

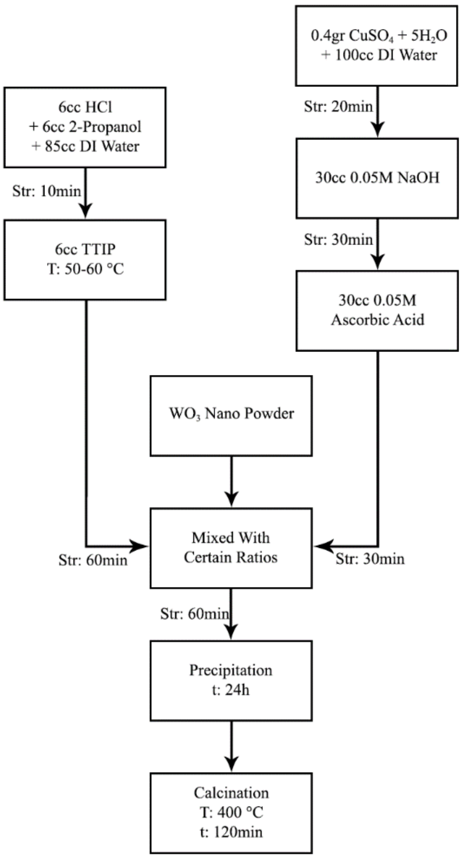


Figure 1. Flowchart of synthesis of $TiO_2/CuO/WO_3$ ternary composite

diffractometer (Bruker D8) with Cu K_α radiation (λ=1.54056 Å) was used, which shows X-ray diffraction patterns with intensity in terms of diffraction angle (2θ). Field-emission scanning electron microscopy (MAIA3, Tescan) was used to evaluate the microstructure of the samples. EDS and map analyzer capabilities were used to more accurately investigate the presence of elements and how they are distributed. The diffusive reflectance spectra (DRS) of the composites were recorded by a UV-Vis spectrophotometer (Avaspec-2048-TEC) using $BaSO_4$ as a reference in the region from 200 to 900 nm.

Photocatalytic activities were investigated by adding 150 mg/l of composite to 50 ml solutions of MeO (with 5 mg/l initial concentration). At first, solution was stirred for 60 min in full darkness to achieve adsorption-desorption equilibrium. UV irradiation from two 6 W lamp (Philips) was then applied to the catalyst containing solution. Samples were then taken out for analysis at the intervals of 30 min. The concentration of dye in the solution was measured spectrophotometrically at the wavelength of the maximum absorbance (λ_{max}: 612 nm).

3. RESULTS AND DISCUSSIONS

The diffraction pattern of TiO_2/10%CuO binary samples and 15WTC ternary samples is shown in Figure 2. In both patterns, the anatase (JCPDS 21-1272) and rutile (JCPDS 21-1276) peaks can be seen well. In the binary sample, CuO phase peaks appeared, but in the ternary sample, due to the low CuO value, the peak was not seen. In the pattern of the ternary sample, the peaks of the orthrombic phase WO_3 (JCPDS 20-1324) are identified. Ke et al. [9] reported that in the TiO_2/WO_3 composite the conversion of the anatase phase to rutile occurs at lower temperatures. WO_3 leads to the formation of W^{+5} and excess oxygen vacancies by the ability to absorb electrons from the TiO_2 conduction band [9, 16]. These oxygen vacancies accelerate the phase transformation in TiO_2 from anatase to rutile. Akhlaghian et al. [29] were observed WO_3 effect in the reduction of anatase phase transformation to rutile phase.

The presence of rutile peaks in Figure 2b may be due to this. On the other hand, the presence of CuO does not cause a significant change in the size of anatase and rutile crystals and their transformation [25].

Figure 3 shows the FESEM and EDS images of TiO_2/CuO binary and 15WTC ternary samples. Figure 3a indicates relatively spherical particles approximately 15-30 nm diameter, and EDS Figure 3c confirms the presence of three elements Ti, Cu, and O. The particle morphology of the 15WTC ternary sample is shown in Figure 3b. As can be seen, TiO_2/CuO nanoparticles have coated the surface of WO_3 coarse particles. EDS in Figure 3d demonstrates the presence of elements W, Ti, Cu and O.

In, The distribution of elements in the ternary sample along with the map images is shown Figure 4. As can be seen, the elements W, Ti and Cu are evenly distributed throughout the sample surface.

Band gap is one of the most important properties of semiconductors in photocatalytic processes and

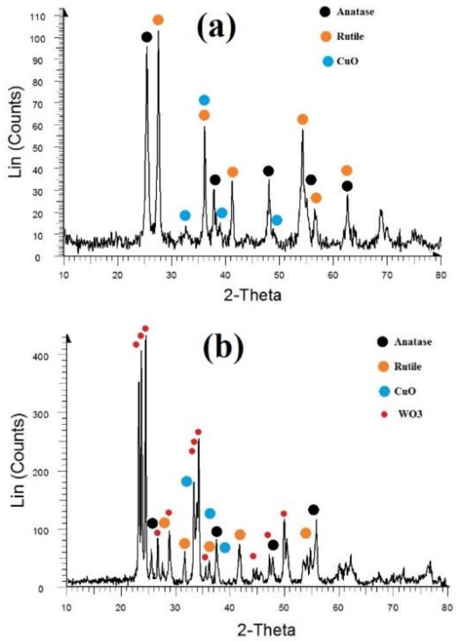


Figure 2. X-ray diffraction pattern of nanocomposite samples (a) binary TiO_2/CuO (b) ternary 15WTC

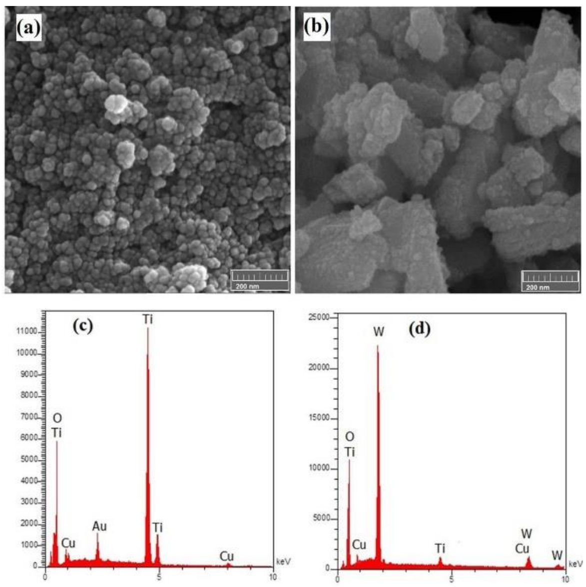


Figure 3. FESEM images of nanocomposite samples (a) binary TiO_2/CuO and (b) ternary 15WTC and EDS spectra of nanocomposite samples (c) binary TiO_2/CuO and (d) ternary 15WTC

applications. Figure 5 shows the DRS analysis results including the absorption spectrum (Figure 5a) and how to determine the band gap (Figure 5b). The value of optical band gap obtained from the diagrams is represented in Table 1. The band gap of the samples was obtained using the kubelka-Munk relationship from the absorption spectrum [25]:

$$(\alpha h\nu) = \beta (h\nu - E_g)^n \tag{1}$$

where E_g is the sample band gap energy (eV), ν is the light frequency (s^{-1}), h is the Planck constant (J.s), β is the absorption constant and α is the absorption coefficient. The value of index n is considered to be 1.2, 3.2 and 2 for direct transition, forbidden direct transition or indirect transition, respectively. The band gap can be determined by extrapolating the linear portion of the $(\alpha h\nu)^n$-hν curve. n=1/2 value better defines our composites [25].

It should be noted that the band gap energy of TiO_2, CuO and WO_3 are 3.20, 1.70 and 2.70, respectively [30]. According to the results, the addition of other compounds to TiO_2 has reduced the band gap energy. For example, the band gap value has been reduced to 2.95 eV for TiO_2/10%CuO. A shift in the absorption edge for TiO_2/CuO composites with CuO is shown to be possibly related to the formation of a defect levels in an energy range in TiO_2 [31].

Addition of WO_3 to the binary compound further reduces the band gap. Baia et al. [32] in the presence of WO_3, were only able to reduce the gap of composite to3.02 eV. Therefore, in order to further reduce the band gap energy, the presence of both components is required. The lowest band gap energy (2.66 eV) was obtained for the 15WTC sample, and then by adding more WO_3 value, due to the fact that a higher level of the TC compound was covered; the ability to absorb the compound decreased, resulting in an increase in the band gap.

TABLE 1. The band gap of samples

Samples	Band gap energy, Eg (eV)
TiO_2	3.20*
TC	2.95
5WTC	2.70
10WTC	2.68
15WTC	2.66
20WTC	2.71

* ref. [25]

Table 2 presents the edge of the conduction band and edge of the valance band for TiO_2, CuO and WO_3 [30]. Because the conduction band of tungsten oxide is lower than that of TiO_2, electron transfer from titanium particles to WO_3 is possible. This action effectively separates the charge carriers and increases their lifetime. In the case of

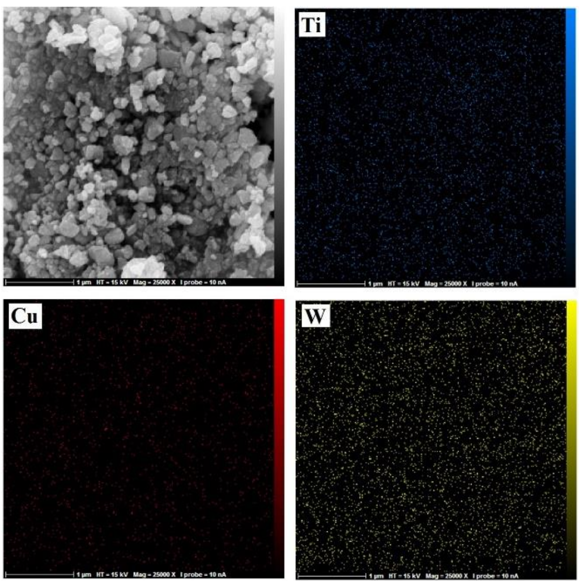
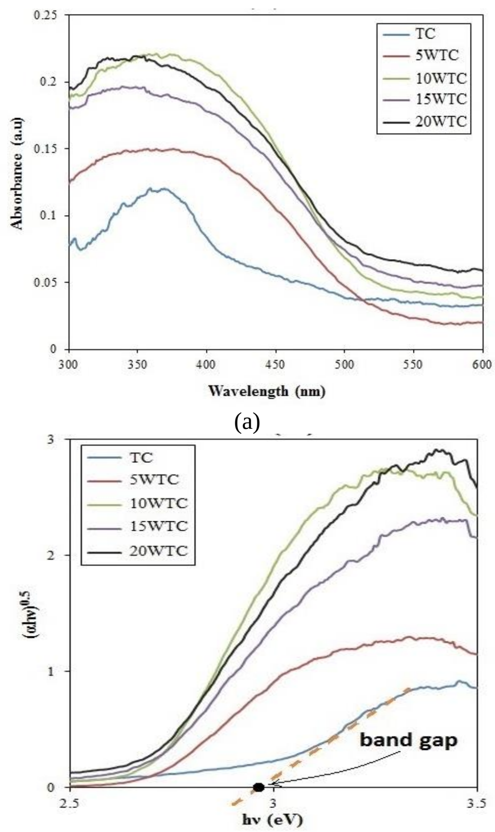


Figure 4. Map images of the distribution of Ti, W and Cu elements in a 15WTC ternary sample



(b)

Figure 5. synthesized nanocomposites (a) UV-Vis diffuse reflectance spectra (b) Tauc plot obtained from UV-Vis DRS spectra

TABLE 2. valance and conduction band edge of different semiconductor [30]

	Conduction Band edge (eV)	Valence Band edge (eV)
TiO_2	-4.21	-1.01
CuO	-4.96	-3.26
WO_3	-5.24	-2.54

TiO_2/WO_3 composition, due to the lower valance band of WO_3 than TiO_2, the transfer of holes in WO_3 is possible. In the case of CuO, the unequilibrium transfer of charge carriers at the TiO_2/CuO junction causes holes to move from TiO_2 to CuO and electrons to move from CuO to TiO_2.

In the case of the $TiO_2/CuO/WO_3$ ternary compound, UV light excites electrons in the conduction band WO_3 and CuO, which are transferred to the conduction band TiO_2. On the other hand, the holes travel in the opposite direction and migrate from the TiO_2 valence band to the WO_3 and CuO valence bands. This migratations of charge carriers restrict their recombination rate and thus enhances the separation of electron-hole pair. The photo-generated electrons can be trapped by oxygen molecules in the organic solution to form superoxide radical anions ($^{\bullet}O_2^-$), which can effectively degradate organic pollutants. These holes convert the water molecules into $OH^{\bullet}$ and react with organic pollutants to genrate H_2O and CO.

Figure 6 shows the function of the compounds in removing methylene orange dye. The photocatalytic performance kinetics of the samples can be evaluated according to the following relation and rate constant comparison [17]:

$$-\ln\left(\frac{C}{C_0}\right) = k_{app}t \qquad (2)$$

where C_0 is the initial concentration of dye, and k_{app} is the apparent constant (min^{-1}). Investigating the changes in ln

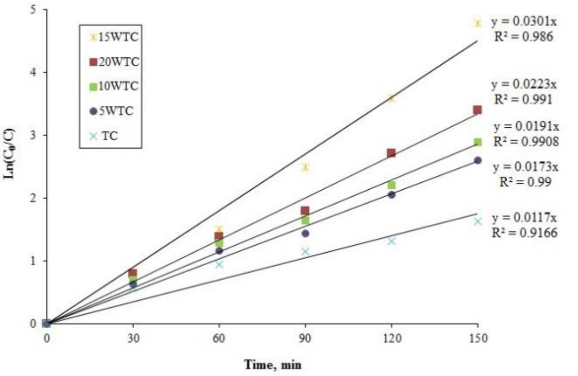


Figure 6. Linear correlation between reaction time and logarithm of relative concentration of methylene orange (ln C_0/C)

(C/C_0) over time for different samples, it is observed that the addition of CuO and WO_3 to the TiO_2 constant speed is improved. The highest rate constant is for the 15WTC sample and is 0.0301 min^{-1}. Akhlaghian et al. [29] in a study showed that the 28.11% CuO/2.1%WO_3/TiO_2 composition was very successful in phenol photodegradation and had a rate constant of 0.0621 min^{-1}. These results indicate that the charge transfer between the compounds and an increase in electron-hole life, their photocatalytic performance is improved.

4. CONCLUSIONS

In this study, ternary $TiO_2/CuO/WO_3$ composites were synthesized and evaluated by different analyzes (XRD, FESEM, DRS and etc.). The results of XRD and FESEM analysis showed purity and uniform distribution of elements. With the production of the ternary omposites, the band gap decreased. Due to the difference in the edge of the conduction band and the valance band, after the production of excited charge carriers with light, electrons and holes are moved at the junction of these semiconductors. This will increase their lifetime and give them a greater chance of participating in redox reactions to remove water pollutions. The results of methylene orange dye removal showed that the ternary composite TiO_2/10%CuO with 15%WO_3 and 2.66 eV band gap, had the highest performance.

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Persian Abstract

چکیده

حذف فتوکاتالیستی آلودگیهای آب و هوا، امروزه بسیار مورد توجه قرار گرفته است. فتوکاتالیست‌های زیادی بر پایه نیمه هادی‌ها تولید شده و مورد استعمال قرار گرفته است. برای رفع مشکلات نیمه هادی‌ها از جمله گاف انرژی بالا و طول عمر پایین حامل‌های بار (الکترون–حفره)، ترکیبات دو جزئی و حتی سه جزئی آنها تولید شده است. در این پژوهش، ترکیب سه جزیئ $TiO_2/CuO/WO_3$، با افزودن نانوذرات WO_3 به TiO_2/CuO سنتز شده است. خواص ساختاری و عملکرد آنها با حذف رنگ متیلن نارنجی مورد ارزیابی قرار گرفت. نتایج آنالیز پراش پرتو X و میکروسکوپ الکترونی روبشی، خالص بودن و توزیع یکنواخت عناصر را نشان داد. ترکیب $TiO_2/10\%CuO$ با $15\%WO_3$ و گاف انرژی 2/66 الکترون ولت بیشترین نرخ حذف رنگ را نشان داد.