The Addition of Graphene and Magnetite Materials in TiO$_2$/CuO Catalyst for Enhancing Photosonocatalytic Performance and Reusability

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Abstract. In the present study, TiO$_2$/CuO with the addition of graphene and magnetite materials were investigated as a catalyst for waste water removal through the photosonocatalytic process. TiO$_2$/CuO/graphene and Fe$_3$O$_4$/TiO$_2$/CuO/graphene were synthesized by using the sol-gel method. Their physical properties were characterized by using X-ray Diffraction, Fourier Transform Infra-red Spectroscopy, Thermogravimetric Analysis, Transmission Electron Microscope, and Brunauer Emmet Teller (BET) surface area analyzer. The Photosonocatalytic activity was examined under visible light irradiation and 40 kHz ultrasound frequency with methyl orange (MO) as a model of organic pollutant. Compared to photocatalytic and sonocatalytic process, photosonocatalytic activity can improve the degradation process due to a synergistic effect between photocatalytic and sonocatalytic process at the same time. The addition of graphene materials can improve the charge carrier separation and prevent recombination electron and holes. Therefore, the photosonocatalytic performance increases significantly with the addition of graphene materials. The addition of magnetite materials is not only can enhance the photosonocatalytic performance but also can improve the separation process for reuse the catalyst. The photosonocatalytic mechanism was correlated with their physical properties and visible as well as ultrasound irradiation.

Keywords: Graphene, magnetite, TiO/CuO, photosonocatalytic.

1. Introduction
Semiconductor materials have been considered as promising photocatalyst materials for removal of organic dye from the environment. Among many others materials, the pioneer photocatalyst materials (TiO$_2$) still attract much attention due to its outstanding performance in the photocatalytic activity [1-2]. TiO$_2$ has excellent properties such as low cost, eco-friendly, and high stability [3]. However, TiO$_2$ has a limitation due to the high rate recombination electron and holes. Moreover, TiO$_2$ with direct band gap 3.2 eV can only be activated by UV light irradiation which takes 4% from the sunlight irradiation [4]. For practical application, it is crucial to modify or create photocatalyst that can be activated not only by UV light irradiation but also under visible light irradiation. Therefore, it is important to modify the TiO$_2$ semiconductor photocatalyst to extend and improve its photocatalytic performance.
To modify TiO₂ properties, they can be coupled with other materials. Many reports have proven that coupled TiO₂ with another semiconductor can enhance the photocatalytic performance and also extend the activation energy to visible light irradiation [5]. Among other semiconductors, CuO has been chosen as suitably coupled materials with TiO₂ due to its proper energy band position that allowed each charge carrier to transfer from one semiconductor to another [6-7]. It will impact the prolonged charge carrier recombination, and the photocatalytic activity can be enhanced. Recently, the carbon materials have been known as promising materials to support the photocatalytic performance due to its unique properties such as (1) high charge carrier mobility, (2) high thermal conductivity and (3) high specific surface area. Those properties are vital in improving photocatalytic performance [8-9].

Separation photocatalyst is another challenge for enhancing the efficiency of the photocatalyst; there are many methods of the separation process of a catalyst such as centrifugation and filtration [10]. However, those methods are expensive and complex process. The use of magnetic separation process offers high efficiency with low cost and simple operation. Magnetic separation process needs magnetic external and also magnetic catalyst inside the solution to attract the catalyst by magnetic separation. Therefore, the incorporation of magnetic materials in the photocatalyst is very promising in separation efficiency. Magnetite (Fe₃O₄) has been considered as supported photocatalyst due to high adsorption capacity, unique magnetic properties, and can prolong charge carrier recombination.

Many researchers have reported that the photocatalytic activity still has a limitation due to the low light penetration ability and agglomeration of particles [11]. The addition of ultrasonic wave in the photocatalytic experiment has been considered as the best solution to overcome the limitation. Ultrasonic wave has better penetration ability compared to light wave in any water medium. Even the existence of ultrasonic wave can promote dispersion of catalyst, and the agglomeration of particles can be prevented [11].

Based on the explanation above, in this work TiO₂/CuO modified by graphene and magnetite material is used as a catalyst for removing methyl orange as a model of organic pollutant. The physical properties of the samples were characterized by using X-ray diffraction (XRD), Fourier transforms infrared spectroscopy (FT-IR), transmission electron microscope (TEM), Thermogravimetric analysis (TGA), and brenneur-Emmet-Teller (BET) surface area analysis. The removal ability of the sample was carried out by using the photosonocatalytic method. The reusability and separation of catalyst were also investigated.

2. Experimental Method

All reagents we used were copper sulfate pentahydrate (Cu(SO₄)₂·5H₂O), Iron sulfate heptahydrate Fe(SO₄)₂·7H₂O, Titanium dioxide (TiO₂), Sodium hydroxide (NaOH), Ethanol, ethylene glycol were purchased from Merck, while graphene was purchased from Angstrom materials. All reagents were used without further purifications.

Fe₃O₄ and CuO were synthesized based on our previous reports [12]. TiO₂/CuO was synthesized by using the sol-gel method. In the typical process, TiO₂ were dissolved in water, and then NaOH solution was added slowly into the TiO₂ solution. CuO nanoparticles were dispersed in water and poured into the above solution. The reaction condition was kept at 80 ⁰C for 2h, and then the precipitates were collected through centrifugation process. The final product was heated at 100 ⁰C for 1 hours. The addition of Fe₃O₄ was done by pouring Fe₃O₄ dispersion in the above solution.

The graphene addition was carried out by using co-precipitation method. Typically graphene was dispersed in water and ethanol mixture through ultrasonic treatment. Each TiO₂/CuO and Fe₃O₄/TiO₂/CuO nanocomposites were immersed in the graphene dispersion and stirred by using magnetic stirrer. After stirring process, the mixture was heated at 120 ⁰C for 3 hours. Finally, the product was collected by using centrifugation process and dried under vacuum condition.

The all prepared samples were characterized by some measurements such as X-Ray diffractions (XRD) using Rigaku Minflex 600 operated at a voltage and current of 30 kV and 150 mA, respectively. Fourier Transform infra-red spectroscopy was investigated by using Shimadzu prestige
with Potassium Dichromate (KBr) as a reference, Thermogravimetric analysis (TGA) measurement was performed by using Rigaku Thermo Plus EVO2 TG8121 under argon atmosphere, and BET surface area was analyzed by using Nova Quantachrome 2000 and transmission electron microscope were characterized by using TEM FEI Tecnai G2 Super Twin. Photosonocatalytic activity was tested on the degradation of methyl orange from the aqueous solution. An amount of 0.03 g catalyst were immersed in 100 mL beaker glass containing 20 mg/L methyl orange concentration. Prior the irradiation, the adsorption process was performed for 4 hours to ensure equilibrium stage of adsorption-desorption. After the adsorption process, the samples were irradiated by using 40 kHz ultrasound and 40 W visible light irradiation simultaneously. Every 15 minutes the methyl orange solution was carried, and its absorbance was measured by using UV-Vis absorbance spectroscopy.

3. Results and Discussion

Figure 1. (a) XRD spectra of Fe₃O₄, CuO, TiO₂ nanoparticles, graphene, TiO₂/CuO, TiO₂/CuO/graphene, and Fe₃O₄/TiO₂/CuO/graphene. (b) FT-IR spectra of TiO₂/CuO, TiO₂/CuO/graphene, and Fe₃O₄/TiO₂/CuO/graphene

Table 1. Lattice parameter and grain size of Fe₃O₄, CuO, TiO₂ nanoparticles, graphene, TiO₂/CuO, TiO₂/CuO/graphene, and Fe₃O₄/TiO₂/CuO/graphene,

| Sample                  | Lattice parameter (Å) | Grain Size (nm) |
|-------------------------|-----------------------|-----------------|
|                         | Fe₃O₄ | TiO₂ | CuO | Fe₃O₄ | TiO₂ | CuO |
| Fe₃O₄                   | 8.363 | -    | -   | -     | -    | -   |
| CuO                     | -     | -    | -   | 4.691 | 3.425| 5.138|
| TiO₂                    | -     | 3.795| 9.525| -     | -    | -   |
| TiO₂/CuO                | -     | 3.792| 9.521| 4.683 | 3.425| 5.134|
| TiO₂/CuO/graphene       | -     | 3.786| 9.516| 4.612 | 3.428| 5.167|
| Fe₃O₄/TiO₂/CuO/graphene| 8.361 | 3.782| 9.510| 4.602 | 3.437| 5.225|

Figure 1a shows the XRD spectra of TiO₂/CuO with the addition of magnetite and graphene. The XRD spectra of Fe₃O₄, CuO, TiO₂, graphene and CuO/TiO₂ were plotted as a comparison. From the XRD spectra of TiO₂/CuO with the addition graphene, several peaks could be found that could correspond to the existence of monoclinic structures from CuO at 2θ ≈ 38° (220), and anatase
structures from TiO$_2$ nanoparticles at 2θ $\approx 26^\circ$ (101) and 48$^\circ$ (004). Moreover, with the incorporation of magnetite material in the nanocomposites, several peaks at 2θ $\approx 30$ (220), 36$^\circ$ (311), and 44$^\circ$ (400) which correspond to the existence of cubic spinel structure of Fe$_3$O$_4$. The presence of graphene could not be detected by using XRD measurement due to the small amount of graphene and also the broad XRD peak of graphene. The lattice parameter and grain size of the samples were calculated by using Rietveld refinement method and debye Scherrer equation. The results are listed in Table 1. The result indicates that there are no significant differences between the lattice parameters of each nanocomposites component compared to its pure nanoparticles.

The molecular vibration of the sample was analyzed by using FT-IR measurement, and the results were plotted in Figure 1b. As a comparison, the FT-IR spectra of graphene, as well as CuO/TiO$_2$, are also plotted in the figures. From the FT-IR measurement, the existence of graphene could be detected at wavenumber of 1050 and 1621 cm$^{-1}$ which could be attributed to the molecular vibrations from C-O and C=C vibrational mode, respectively [13]. As can be seen from the figure the vibrational mode of TiO$_2$/CuO does not change with the incorporation of graphene. The vibrational mode around 400-700 cm$^{-1}$ could be attributed to the existence of Cu-O and Ti-O-Ti vibration [14-15]. The incorporation of magnetite material on the nanocomposite resulted in the sharp peak around 500-700 cm$^{-1}$ that could be attributed to the existence of Fe-O vibration [16]. The broad peak around 3000-3400 cm$^{-1}$ express the O-H vibrations from water molecules [16].

Thermal degradation of samples was measured to analyze the stability of the samples. Thermal stability was recorded at room temperature until 1000 $^\circ$C. Figure 2 shows the TGA measurement of Fe$_3$O$_4$/TiO$_2$/CuO/graphene. As a comparison, the TGA measurement of TiO$_2$/CuO and TiO$_2$/CuO/graphene composites were also performed. From the figures, we can find that the TiO$_2$/CuO performed good stability until 1000 $^\circ$C. However, the incorporation of graphene the thermal stability of samples slightly decreased. At the region of 25 $^\circ$C until 100 $^\circ$C the thermal degradation could be due to the desorption of physically adsorbed water and residual solvent [16]. The thermal degradation from 400 $^\circ$C–850 $^\circ$C could be attributed to the combustion of carbon materials, and at 850 $^\circ$C to 1000 $^\circ$C the thermal degradation could be due to the phase transformation between CuO to Cu$_2$O.

The surface area of the samples was measured by using BET measurement. The results were listed in Table 2. The specific surface area of CuO/TiO$_2$ is 5.78 m$^2$/g. The incorporation of graphene enhances the specific surface area of the samples until 45.43 m$^2$/g, however with the inclusion of magnetite Fe$_3$O$_4$ the specific surface area of the sample decreased to 34.32 m$^2$/g. The specific surface
area is important in catalytic performance. The presence of surface areas is favorable to absorb pollutants, harvest light and separate the photogenerated electron-hole pairs, which are factors for the promotion of catalytic activity.

Table 2. A surface area analysis of TiO$_2$/CuO, TiO$_2$/CuO/graphene, and Fe$_3$O$_4$/TiO$_2$/CuO/graphene.

| Sample                        | Surface area (m$^2$/g) |
|-------------------------------|------------------------|
| TiO$_2$/CuO                   | 5.78                   |
| TiO$_2$/CuO/graphene          | 45.43                  |
| Fe$_3$O$_4$/TiO$_2$/CuO/graphene | 34.32                  |

Figure 3. (a)TEM and (b) SAED pattern Fe$_3$O$_4$/TiO$_2$/CuO/graphene.

The morphology of the samples were investigated by using TEM measurement. Figure 3 represents the TEM and SAED pattern of Fe$_3$O$_4$/TiO$_2$/CuO/graphene. As can be seen from the figure that the material Fe$_3$O$_4$, TiO$_2$, and CuO could be dispersed in the graphene sheets. The SAED pattern indicates that the samples pose good crystallinity.

Figure 4. (a) Adsorption capacity and (b) photosonocatalytic activity of TiO$_2$/CuO, TiO$_2$/CuO/graphene and Fe$_3$O$_4$/TiO$_2$/CuO/graphene
Before investigating the photosonocatalytic performance, we evaluated the adsorption ability of the samples. The adsorption experiment was represented with adsorption capacity vs. time as can be seen in Figure 4a. The amount of dye adsorbed at different time intervals was calculated by using the following equation:

\[
q_t = \frac{(C_0 - C_t)V}{m}
\]

where \(q_t\) is the amount of dye adsorbed per unit mass of adsorbent (mg/g) at time \(t\) and \(C_t\) is concentration of dye (mg/L) at time \(t\), \(m\) is amount of adsorbent (g), and \(V\) is amount of dye solution (L). The all prepared samples were significantly adsorbed for early 30 min. After 30 min the adsorption ability achieved the equilibrium stage. The adsorption capacity gradually increased with the addition of graphene and Fe\(_3\)O\(_4\). The adsorption capacity was found increased from 10 mg/g to 41 mg/g for CuO/TiO\(_2\) and Fe\(_3\)O\(_4\)/TiO\(_2\)/CuO/graphene respectively. The increase of adsorption ability from Fe\(_3\)O\(_4\)/TiO\(_2\)/CuO/graphene is probably due to the higher specific surface area and the higher adsorption capacity of Fe\(_3\)O\(_4\).

According to the adsorption ability of the samples, now we investigated the photosonocatalytic activity for all samples. The result is plotted in Figure 4b. The induction of Fe\(_3\)O\(_4\) and graphene significantly increased the photosonocatalytic activity for removing organic dye from the aqueous solution. TiO\(_2\)/CuO has degradation efficiency about 31%; with the addition of graphene the degradation efficiency increased to 58%. The degradation efficiency further increased with the incorporation of Fe\(_3\)O\(_4\) with the maximum degradation efficiency around 68%. The higher catalytic performance was probably due to the retarding of recombination electron and holes and the enhancement of the specific surface area. The retarding of recombination electron and holes could promote the interaction between holes and electron with water and oxygen molecules, respectively to produce free radicals for attacking the organic dye.

![Figure 5](image_url)

**Figure 5.** (a) photo-, sono-, and photosono-catalytic activity of Fe\(_3\)O\(_4\)/TiO\(_2\)/CuO/graphene. (b) Methyl orange absorbance spectra after photosonocatalytic reaction by using TiO\(_2\)/CuO, TiO\(_2\)/CuO/graphene and Fe\(_3\)O\(_4\)/TiO\(_2\)/CuO/graphene.

Figure 5a represents the comparison between photo-, sono-, and photosono-catalytic performance of Fe\(_3\)O\(_4\)/TiO\(_2\)/CuO/graphene. From the figure, we can found that the photocatalytic activity exhibits lowest degradation ability than sonocatalytic and photosonocatalytic process. It could be due to the lowest light penetration under photocatalytic process [11]. The using ultrasound irradiation has the advantage to penetrate any aqueous medium. Therefore, the degradation ability increased [11].
Moreover, after the combination between both photocatalytic and sonocatalytic process, the degradation ability increased significantly. It indicates that the synergy between photo- and sonocatalytic is very potential for waste water removal.

Figure 5b shows the absorbance spectra vs. wavelength of methyl orange at the different catalyst. According to absorbance spectrum of methyl orange, maximum absorbance is at 465 nm. It can be seen from the figure that the adsorption spectra gradually decreased after photosonocatalytic reaction. It indicates that the methyl orange is degraded by using photosonocatalytic process. The methyl orange absorbance from Fe₃O₄/TiO₂/CuO/graphene exhibits the lowest absorbance spectra indicating the highest degradation ability for removing methyl orange.

![Figure 6](image)

**Figure 6.** (a) Magnetic separation process. (b) Reusability of catalyst

The reusability is also an important parameter for practical application. The reusability experiment was carried out by using the external magnetic bar to collect the magnetic catalyst. The magnetic separation process is depicted in Figure 6a. As can be seen from the figure, the samples could easily be attracted by the presence of an external magnetic bar. It indicates that the magnetic separation process is an effective method for separating catalyst from the solution. After the separation process, the new MB were poured into the beaker glass containing a catalyst. After that, dark process and photosonocatalytic process were repeated for four-times used. The reusability result is plotted in Figure 6b. From the figure, we can see that the samples possess good stability after four-times cycling process.

4. **Conclusion**

The Fe₃O₄/TiO₂/CuO/graphene was successfully synthesized by using the hydrothermal method. The addition of graphene materials could enhance the adsorption and photosonocatalytic performance. The addition of magnetite materials could increase the photosonocatalytic performance as well as the stability of the samples. The enhancement of surface area and retarding or recombination electron and holes are probably the main important aspect of the increasing photosonocatalytic performance. The higher degradation of photosonocatalytic performance compared to photocatalytic and sonocatalytic is due to the synergistic effect of ultrasound and visible light irradiation.

5. **References**

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