Preparation of CeO$_2$/TiO$_2$/NGP composites as efficient catalyst for removal of organic dye using photo-, sono-, and sonophotocatalytic activity

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Abstract. A simple hydrothermal technique was used to incorporate nanographene platelets (NGP) with CeO$_2$/TiO$_2$ composites with different NGP contents. The prepared samples were then evaluated as a heterogeneous catalyst to degrade methylene blue (MB) under visible light irradiation, ultrasonic irradiation, and a combination of the two. The structural and morphological properties of CeO$_2$/TiO$_2$/NGP composites were investigated by X-ray diffraction (XRD). The XRD spectra of CeO$_2$/TiO$_2$/NGP revealed the spectra of NGP, CeO$_2$, and TiO$_2$ nanoparticles indicating the desired combination. Further investigation using TGA measurements show that weight was lost at around 600 °C due to the combustion of carbon. The surface area of the composites was further increased. The prepared CeO$_2$/TiO$_2$–10 wt.% NGP composites were able to degrade MB four times higher than pristine CeO$_2$/TiO$_2$ composites, which may be due to a lower recombination rate; however, further increments of NGP decreased the degradation efficiency.

Keywords: Organic dye, photocatalytic, sonocatalytic, sonophotocatalytic

1. Introduction
The use of dyes as one of the human-made organic pollutants is widely applied in various industries such as food, leather, and textiles. The major environmental pollution in aquatic system can occur with the larger scale and massive development of these industries [1]. The removal of such dyes has attracted intensive research interest; among the various methods employed, heterogeneous catalysts have emerged as the most promising green technology [1, 2]. However, to employ the catalyst effectively using solar energy, it is necessary to provide the catalyst with a band gap of less than about ~2.7 eV. Thus, the design of visible-light-driven catalysts is an active research field.

In the field of environmental remediation, TiO$_2$ has emerged as a promising candidate because of several characteristics such as its low cost, non-toxicity, and good thermal-chemical stability. However, TiO$_2$ has several limitations: (1) a wide band gap of ~3.2 eV and ~3.0 eV for the anatase or rutile phases, respectively, and (2) a high recombination rate of electron–holes [3]. Several strategies have been used to overcome these limitations. One effective strategy is to combine TiO$_2$ with other semiconductor with another semiconductor metal oxide as CeO$_2$ [3, 4]. The special $f$ and $d$ electron...
orbital structures and unique ability to absorb UV light, as well as its high electrical conductivity and large oxygen storage capacity of CeO2 make this material attractive for combination with TiO2 [4, 5].

Graphene has attracted special attention because of its unique structural and electronic characteristics [6]; its notable characteristics include excellent electrical, high mobility, and excellent chemical stability. The combination of graphene and semiconductors enhanced catalytic activity; this may have been due to the effect of graphene on hindering the recombination rate of electron–hole pairs [6].

Accordingly, in this study, the activity of CeO2/TiO2 modified with NGP was studied for catalytic activity under visible irradiation, ultrasonic irradiation, and a combination of the two. To study the effect of NGP, the content of NGP was varied and subjected to various analyses such as X-ray diffraction (XRD) and the Brunner Emmet Teller (BET) technique.

2. Experimental detail

2.1. Materials
The reagents used are manufactured by Merck such as titanium dioxide (TiO2, 99 %), Cerium sulfate pentahydrate (CeSO4·5H2O), ethanol and sodium hydroxide (NaOH). However, nanographene platelets (NGP) in this study used the production of Angstron Materials Inc. All chemicals are used directly without going through further purification since these are already analytical grade. Preparation of the solutions is using deionized water (DI) as a solvent.

2.2. Catalyst preparation
The CeO2 nanoparticles were synthesized using the sol-gel method based on our previous study [7], typically by dissolving CeSO4·5H2O in DI water then added with NaOH solution. The mixture was heated at temperature of 80 °C while stirring for 4 h. The centrifuge separated the mixed precipitate from its solvent. When drying it, a vacuum condition is applied. The dried precipitant then calcined at a temperature of 800 °C.

Dissolving TiO2 in NaOH solution is first step to synthesize TiO2/CeO2. Then the solution is stirred continuously while being heated to a temperature of 80 °C using a magnetic stirrer equipped with a heater. This solution is added with dispersed CeO2 nanoparticles when the temperature was reached 80 °C, then, stirring is continued for 2 h. Washing was performed several times using ethanol and distilled water to the precipitate obtained. The precipitant is then dried after being aged first. The drying process is carried out for 1 h under vacuum at a temperature of 100 °C for 1 h under vacuum. The molar ratio of TiO2 : CeO2 is 1 : 1.

TiO2/CeO2/NGP composites were synthesized using a hydrothermal method based on; in brief, an amount of NGP (5, 10, and 15 wt.%) was mixed in a solution (80 mL DI + 40 mL ethanol) through ultrasonic treatment for 2 h. Then, 1 g of CeO2/TiO2 composites was poured to the mixture while stirring until a homogeneous suspension is created for 2 h. Heating the suspension for 3 h at temperature of 120 °C is performed. The resulting suspension was centrifuged and dried at 70 °C for 12 h to obtain CeO2/TiO2/NGP composites.

2.3. Characterization
The structural and adsorption properties of the samples were characterized using XRD measurements using a Rigaku Miniflex 600 diffractometer (Cu K-α radiation), the BET method, transmission electron microscope (TEM) spectroscopy, and energy dispersive X-ray spectroscopy. The thermal stability of the samples was characterized using thermogravimetric analysis (TGA).

2.4. Catalytic test
The test was conducted using methylene blue (MB) as the organic pollutant. The procedure was as follows: 0.3 gL⁻¹ of the prepared composites was added to 100 mL of MB (20 mgL⁻¹), then stirred until
the adsorption and desorption equilibrium reached between the MB molecules and the catalyst surface. Stirring is performed for 30 min in dark conditions. Then the catalyst's catalytic activity in degrading MB was evaluated through exposure to UV radiation, ultrasound, and both radiation sources after this referred to as photocatalytic, sonocatalytic, and sonophotocatalytic activity. The solution was taken and analyzed using a UV-Vis spectrometer at specific time intervals. The percentage of MB degraded for a particular time is obtained from equation 1:

\[
\% \text{ degradation} = \left(1 - \frac{C_t}{C_0}\right) \times 100\%
\]

where \(C\) is the MB concentration at initial (\(C_0\)) and after irradiation exposure for time \(t\) (\(C_t\)).

3. Results and discussion

The photo-, sono-, and sonophotocatalytic activity of CeO\(_2\)/TiO\(_2\) composites were evaluated by the degradation of MB; the results are shown in figure 1a. As can be seen, the incorporation of NGP in CeO\(_2\)/TiO\(_2\) composites could enhance the degradation efficiency in all catalytic activity. However, an increment of 15 wt.% of NGP decreased the degradation efficiency in all catalytic activity; this could be explained by the phenomenon of the shielding effect, whereby further increments of NGP materials block the incidental light falling upon CeO\(_2\)/TiO\(_2\) composites. From figure 1, we can also see that the degradation efficiency follows the order: sonophotocatalytic<sonocatalytic<photocatalytic, indicating that by combining both forms of irradiation (UV and ultrasound) may better produce OH radicals as reactive species that could degrade MB [8]. For a better understanding of catalytic activity, other experiments were evaluated: the effect of dosage, the effect of MB concentration, and the effect of scavengers with the NGP contains 10 wt.%.

The effect of dosage in all catalytic activity was studied by varying it from 0.1 to 0.4 gL\(^{-1}\) in increments of 0.1 gL\(^{-1}\); the results are shown in figure 1b. The degradation efficiency in all catalytic activity increased as the dosage increased from 0.1 to 0.3 gL\(^{-1}\). However, the further increment to 0.4 gL\(^{-1}\) decreased the degradation efficiency; this may be due to the particles shielding
and thus reducing the amount of irradiation light transmitted [9, 10]. Thus, we obtained that 0.3 gL⁻¹ of the composite was optimum and was used in all other experiments.

From figure 2a, we can see the effect of initial concentration of MB was studied. The result reveals that increments in the MB concentration decreased degradation efficiency [9]. This result may be due to the increase in MB molecules in the aqueous solution making the degradation of MB more difficult. Furthermore, increments in MB concentration block the active sites of CeO₂/TiO₂/NGP, which prevents irradiation light to penetrate the surface of the composites [9, 11].

In order to further study the process of catalytic activity in photo-, sono-, and sonophotocatalytic activity, control experiments employing several scavengers—di-amonium oxalate, sodium sulfate, and tertiobutyl alcohol as hole, electron, and hydroxyl radical scavengers, respectively—were conducted. Figure 2b shows the results that the active species of all catalytic activity followed the same orders: hole > hydroxyl radicals > electron. This indicated that hole and hydroxyl radicals play an important role in all catalytic activity.

The phase and crystal structure of TiO₂/CeO₂/NGP composites with different wt.% of NGP is shown in figure 3. All samples exhibit several peaks that could be indexed as anatase TiO₂ (2θ = 25.3°, 37.9°, 48.1°, 54.0°, 55.0°, and 62.8°) [12] and the crystalline cubic phase of CeO₂ (2θ = 28.8°, 33.4°, 47.6°, and 56.6°) [13]. The incorporation of NGP could be indexed in 2θ = 26.4°; as can be seen, incrementing NGP content increased the peaks’ intensity. No additional peaks related to impurities was detected, which confirms that all samples consist of CeO₂, TiO₂, and NGP materials.

The thermal stability of CeO₂/TiO₂/NGP composites with various NGP contents was detected using TGA measurement. Based on the measurement results in figure 4, CeO₂/TiO₂ composites exhibit good thermal stability up to a temperature of 1000 °C; after the incorporation of NGP by 5, 10, and 15 wt.% a mass loss occurred of ~4, ~9, and ~15 %, respectively. Such significant loss occurred due to the combustion of carbon from NGP materials [14]. The mass loss was in accordance with theoretical values of NGP mass in the experimental process.

The TEM image of TiO₂/CeO₂/NGP composite was shown in figure 5. As can be seen from the figure, the TEM image of TiO₂/CeO₂/NGP composites consists of different sizes of particles; this could be attributed to the different sizes of TiO₂ and CeO₂. As can be seen from the figure, the particles of TiO₂ and CeO₂ were dispersed in the NGP layers, which confirms the formation of TiO₂/CeO₂/NGP composites. The EDX spectrum of TiO₂/CeO₂/NGP composites was plotted in figure 6. The EDX spectra of TiO₂/CeO₂/NGP revealed that the atomic composition of the prepared

Figure 2. (a) Effect of MB concentration in catalytic performance of CeO₂/TiO₂—10 wt.% NGP. (b) Effect of scavengers in catalytic performance of CeO₂/TiO₂—10 wt.% NGP.
samples consists of Ti (Titanium), Ce (Cerium), C (Carbon). The Cu atom detected by the EDX measurement is due to the copper grid used in the measurement. It indicates that the sample TiO$_2$/CeO$_2$/NGP composite was successfully formed.

The surface areas from the BET measurements of TiO$_2$/CeO$_2$/NGP with different NGP weight percentages are shown in figure 7. From the BET measurement, it can be seen that the incorporation of NGP increased the specific surface area of the samples. The high specific surface area may play an important role in absorbing a large amount of dye [15]; however, in catalytic activity, various factors influence the results such as the type of catalyst, structure, and morphology.

To understand the catalytic activity exhibited by TiO$_2$/CeO$_2$/NGP composites, the correlation of degradation and physical properties were proposed as follows: from the XRD, BET, and TGA measurements, we could confirm the existence of CeO$_2$, TiO$_2$, and NGP in the samples. In accordance with the theory, TiO$_2$ combined with CeO$_2$ may produce a heterojunction due to combination of
Figure 7. Specific surface area of TiO$_2$/CeO$_2$ and TiO$_2$/CeO$_2$/NGP composites.

p-type (TiO$_2$) and n-type (CeO$_2$) semiconductors in which the separation efficiency of electron–hole pairs is increased and recombination inhibited. The incorporation of NGP materials [13, 16] increased the specific surface area, and NGP materials could act as an electron trapping state, which could inhibit the recombination of electron–hole pairs, indicating the increase in the lifetime of electrons and holes to actively degrade MB molecules [17]. However further increment of NGP created a shielding effect which decreased the degradation efficiency of the composites.

4. Conclusion

In summary, NGP was successfully incorporated into CeO$_2$/TiO$_2$ composites using a simple hydrothermal method to create CeO$_2$/TiO$_2$/NGP composites. The photo-, sono-, and sonophotocatalytic activity showed that the incorporation of NGP increased degradation efficiency. However, we obtained an optimum incorporation of NGP at 10 wt.%. The catalytic activity of all samples followed the order: sonophotocatalytic>sonocatalytic> photocatalytic, and the maximum dosage and main active species were 0.3 gL$^{-1}$ and hole, respectively. From the initial concentration experiments, we found that increasing the initial concentration decreased the degradation efficiency.

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