Preparation and catalytic performance of ZrO$_2$ - nanographene platelets composites

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Abstract. The ZrO$_2$/Nanographene platelets (NGP) composites with different NGP weight percents were successfully synthesized using two-step methods (sol-gel followed by co-precipitation methods). The structural properties of the composites were analyzed using X-Ray Diffraction (XRD), Energy Dispersive X-Ray (EDX), Transmission Electron Microscope (TEM), and Thermalgravimetric Analysis (TGA). The presence of NGP in the composites confirms by the graphitic-like structure in the XRD and layer-like structure in the TEM. Thermal stability of the composites tends to reduce with the incorporation of NGP. The catalytic performances of the composites were evaluated by three catalytic processes. The degradation of methylene blue as a model pollutant by the composites are monitored using UV-Vis Spectroscopy. The result shows that ZrO$_2$ with 10 wt% of NGP exhibits the highest performance for all of three processes. The scavenger experiment shows that hole acts as an active species that play a role in the catalytic process of the composites.

1. Introduction
The waste water and dyes of the textile industry contain organic dye substance that may cause serious damage to the environment. Moreover, it difficult to be destroyed using traditional waste water treatment [1]. One of commonly-used dye substance is methylene blue (MB), a dangerous cationic with mutagen and carcinogen properties as well as resistant to biological decomposition [2]. There are various techniques to decompose the dye substances, such as electrochemical treatment [3], chemical oxidation [4] and surface adsorption [5]. Other methods to decompose dye substances are using photocatalytic and sono-catalytic. These two techniques are a promising method in decomposing dye substances because of their practical application and do not create any secondary pollutant [6-8].

Use of metal oxide semiconductor (MOS) as a catalyst in catalytic activities has attracted researchers’ attention due to it can exhibit good performance in decomposing and destroying organic pollutants to decontaminate water [9]. Among the various of MOS, Zirconium oxide (ZrO$_2$) is an n type of semiconductor which recently has attracted the attention because of its unique properties such as high photosensitivity, high stability, non-toxic, high melting point, and good adsorption [10,11]. Therefore, ZrO$_2$ has various applications in many field, such as gas sensor, catalyst or supporting catalyst, photocatalyst and waste water treatment [12-14]. In the previous report, ZrO$_2$ as a catalyst has successfully degrade organic dye substance [15]. It indicates that ZrO$_2$ has the potency to be applied as...
a catalyst for catalytic activities. Nevertheless, catalytic performance of ZrO$_2$ in degrading organic dye substance is relatively low. This is because of fast recombination rate of electron-hole pairs [16]. To deal with this issue, we can combine metal oxide with graphene material. The properties of graphene as electron transport channel could prevent recombination of electron-hole pairs. Moreover, graphene could increase the process of charge separation and improve the adsorptive capacity in catalyst surface to enhance the catalytic performance [17].

The focus of this study is to investigate the catalyst’s capacity in degrading MB as the pollutant model and the effect of adding NGP on improvement of catalytic performance in the photocatalytic, sonocatalytic, and photosonocatalytic processes. The scavenger is added to evaluate the behavior of oxidative species that has a role in degrading MB solution.

2. Experimental

**Preparation of ZrO$_2$ nanoparticle:** ZrO$_2$ nanoparticle is synthesized by sol-gel method. The precursor of Zirconium (IV) Chloride (ZrCl$_4$) and Sodium Hydroxide (NaOH) is dissolved into distilled water. Then ZrCl$_4$ solution is poured slowly into NaOH solution under magnetic stirring. The formed gel remains stirred magnetically for 3 hours at the temperature of 80$^\circ$C. Then, the white colloid obtained is centrifuged and rinsed using distilled water and ethanol several times. After the rinsing process, the samples are dried for 12 hours at 120$^\circ$C then calcined for 5 hours at the temperature of 550$^\circ$C. This process will produce ZrO$_2$ nanoparticles.

**Preparation of ZrO$_2$ - NGP composites:** ZrO$_2$ - NGP composites are synthesized by co-precipitation method. The NGP powder is dissolved into distilled water and ethanol. The NGP solution is put into an ultrasonic bath for sonication process for 2 hours to make the suspense homogenous. Afterward, ZrO$_2$ nanoparticle is poured into the NGP solution and stirred magnetically for 1 hour. The solution is heated for 3 hours at the temperature of 120$^\circ$C. The grayish colloid obtained is centrifuged and rinsed using distilled water and ethanol several times. In the final stages, the samples are dried up for 12 hours at the temperature of 70$^\circ$C under the vacuum condition. This produces grayish ZrO$_2$ - NGP composite powder.

**Characterization:** ZrO$_2$ nanoparticles and ZrO$_2$ - NGP composites are characterized by X-Ray Diffraction (XRD) Diffractometer Rigaku Miniflex 600 with the radiation source of Cu-K$_{\alpha}$, wave length $\lambda$=1,5406, Transmission Electron Microscopy (TEM) Tecnai G2 Supertwin with the voltage of 200 kV, Energy Dispersive X-Ray (EDX) Spectroscopy and Thermal Gravimetric Analysis (TGA) Rigaku TG8121 with aluminum oxide (Al$_2$O$_3$) as reference to identify the physical and structural properties of the samples.

**Catalytic experiments:** The photocatalytic, sonocatalytic, and photosonocatalytic activities of the samples are studied in MB degradation. The samples are poured into methylene blue solution and stirred magnetically for 30 minutes under dark condition to reach adsorption/desorption equilibrium between substrate and catalyst. Catalytic activities examination is done for 2 hours after the dark process. At a certain time interval, about 5 mL of suspense is taken from reactor cell and centrifuged to separate the catalyst with MB solution. Then changes in MB concentration are monitored by inspecting the absorption peak at 663 nm using UV-Vis Spectrophotometer. The photocatalytic activity is carried out by irradiating the solution mixture with ultraviolet (UV) light. Two 40-watt UV-C lamps are used as sources of ultraviolet light radiation. Sonocatalytic activity is conducted by giving ultrasonic radiation. Ultrasonic bath with frequency vibration of 40 kHz and power of 150 watts are used as the reactor of ultrasonic radiation. Meanwhile photosonocatalytic activity is performed by combining the photocatalytic process with the sonocatalytic process, namely by giving ultraviolet and ultrasonic radiation at the same time.

**Scavenger experiments:** To analyze the species involved in the process of degradation, the scavenger is examined by adding certain reagents into the MB solution. As the inhibitor for the species of hole,
electron, and hydroxyl radicals (OH\(^\bullet\)), diaminium oxalate (C\(_2\)H\(_8\)N\(_2\)O\(_4\)), sodium sulphate (Na\(_2\)SO\(_4\)), and tert-Butyl alcohol ((CH\(_3\))\(_3\)OH) are used respectively. The same measurements as described above were used.

3. Result and Discussion

As shown in the Figure 1, ZrO\(_2\) diffraction peak at 2\(\theta\) = 30.18\(^\circ\), 35.03\(^\circ\), 50.36\(^\circ\), and 59.94\(^\circ\) are associated with \(\approx [111], [200], [220], \) and [311] planes. These planes indicate the tetragonal phase from ZrO\(_2\). Meanwhile, the peak at 2\(\theta\) = 26.49\(^\circ\) is associated with [002] plane of graphitic-like structure of NGP. The diffraction peak owned by ZrO\(_2\) - NGP can be seen as combination from the tetragonal peak of ZrO\(_2\) and NGP structure without any new peak is existed. This confirms that the desired samples are successfully synthesized. Increased intensity of NGP peak at the XRD pattern of ZrO\(_2\) - NGP samples indicates the more content of NGP in the samples. The average of grain size is calculated using the Debye Scherrer’s formula for [111] plane and the lattice parameter value is refined using the Rietveld refinement. The resulted calculations are presented in Table 1.

The TEM images of ZrO\(_2\) nanoparticles and ZrO\(_2\) - NGP composites are shown in Figure 2. It is seen that there is nanoparticle agglomeration with nearly spherical topography which indicates the existence of ZrO\(_2\). This nanoparticle agglomeration may occur because of high surface energy of ZrO\(_2\) nanoparticle [18]. The existence of NGP in ZrO\(_2\) - NGP composites is indicated in Figure 2 (b) in the shape similar to layer-like. Based on TEM analysis, the average of grain size is around 13 nm. The result is consistent with the result shown in XRD analysis.

The elements of these samples are analyzed using EDX. The EDX spectrum shows that ZrO\(_2\) sample consists of the elements of Zr, O and Cu. The existence of Cu element in EDX spectrum is derived from grids during measurement. Meanwhile in ZrO\(_2\) - NGP samples there is a carbon (C) element which indicates the existence of NGP in the sample. No other elements indicate that the synthesized samples have good purity. Thermal stability of ZrO\(_2\) and ZrO\(_2\) - NGP samples is represented with the loss of mass

![Figure 1. XRD pattern of NGP, ZrO\(_2\), and ZrO\(_2\) - NGP with different NGP weight percents.](image)

| Sample          | Lattice Parameter (Å) | NGP Parameter (Å) | \(<D>\) (nm) |
|-----------------|-----------------------|-------------------|--------------|
| ZrO\(_2\)       | a=b\(\neq\)c          | -                 | 13.59        |
| ZrO\(_2\) - 5 wt% NGP | 3.612 ; 5.153         | 3.635             | 12.97        |
| ZrO\(_2\) - 10 wt% NGP | 3.614 ; 5.156         | 3.637             | 12.41        |
| ZrO\(_2\) - 15 wt% NGP | 3.615 ; 5.157         | 3.638             | 12.02        |
in thermal gravimetric analysis indicated in Figure 3b. Both ZrO$_2$ and ZrO$_2$ - NGP experience loss of mass by around 100°C. This loss occurs due to possibly desorption (removal) of water molecule which is physically attached to the nanomaterial. At the temperature of around 670°C, ZrO$_2$ - NGP samples significantly experience loss of mass indicated with the combustion of NGP.

![Figure 2. TEM of (a) ZrO$_2$ and (b) ZrO$_2$ - NGP.](image)

In order to evaluate the ability of catalyst to degrade MB, photocatalytic, sonocatalytic and photosonocatalytic were performed. All catalytic activity measurements are performed under room temperature with the catalyst dosage of 0.3 g/L. In Figure 4 (a), each catalyst in the photosonocatalytic process exhibit the highest degradation efficiency followed by sonocatalytic and photocatalytic processes. Increased degradation efficiency can also be seen for sample with the addition of NGP. The increasing of degradation efficiency occurs due to NGP as a graphene material can reduce the recombination rate of electron-hole pairs, and it also able to increase the charge transfer between metal oxide and dye molecule, as well as improve the adsorptive capacity in catalyst surface [17,19,20]. Moreover, ZrO$_2$ - 10 wt% NGP is found that exhibit the highest degradation efficiency. Decreased efficiency occurring on ZrO$_2$ - 15 wt% NGP may be caused by excessive addition of NGP composition that may cover the active sites of ZrO$_2$ catalyst. In the process of catalytic activities for 120 minutes, ZrO$_2$ nanoparticle can degrade by 60.6%, 75%, 83.5 % and ZrO$_2$ - 10wt% NGP composites can degrade by 77.3%, 91.7%, 100% each for the photocatalytic, sonocatalytic, and photosonocatalytic process, respectively. The experiment of MB degradation follows the first-order kinetics [21]. The rate of the
constant MB degradation ($K_{app}$) for all samples and catalytic activities are indicated in Figure 4b. The figure confirms that degradation efficiency of ZrO$_2$ nanoparticle increases with the addition of NGP and it achieve maximum at 10 wt% of NGP.

Diamonium oxalate, sodium sulphate, and tert-Butyl alcohol are added to analyze the species that has the role in the process of MB degradation which is useful for inhibiting respectively the species of hole, electron, and hydroxyl radical in photocatalytic, sonocatalytic, and photosonocatalytic as presented in Figure 5. It can be seen that for each catalytic process, the addition of diamonium oxalate can cause highest decrease of degradation efficiency compared to the others. In other words, hole is an oxidative species that plays the most active role in the process of MB degradation. There is a difference in the role of species in the degradation of MB in photocatalytic with sonocatalytic and photosonocatalytic process. In the photocatalytic, the sequence species that play the most role in the process of MB degradation is hole > electron > OH$^\bullet$. Meanwhile for sonocatalytic and photosonocatalytic are hole > OH$^\bullet$ > electron. This is possible because sonocatalystic involves the hot spot process that can increase the OH$^\bullet$ population through pyrolysis of water molecule [22,23].

In evaluating the stability and reusability, the catalyst is used repeatedly for four cycles. At the end of each cycle, the catalyst is separated from MB solution by centrifuged to be re-used under the same MB condition as previously. The result of re-use catalyst in degrading MB are indicated in Figure 6.

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**Figure 4.** The effect of different NGP weight percents: (a) degradation curve, (b) rate constant diagram

**Figure 5.** The effect of addition of various scavenger: (a) ZrO$_2$, (b) ZrO$_2$ - 10 wt% NGP.
can be seen that both ZrO$_2$ and ZrO$_2$ - NGP samples do not experience significantly-decreased degradation efficiency for each cycle. It indicates that the catalyst has good stability and reusability capability.

4. Conclusion

ZrO$_2$ - NGP composites have been successfully synthesized by sol-gel method followed by co-precipitation that confirmed with the XRD, TEM, EDX, and TGA characterizations. The degradation efficiency of catalytic activities improves with the NGP addition. The sample with the additional 10 wt% of NGP exhibit the best catalytic performance. ZrO$_2$ composites - 10 wt% can degrade MB solution by 77.3%, 91.7%, 100% for photocatalytic, sonocatalytic, and photosonocatalytic processes, respectively. In the scavenger experiment, the hole is known as the species that plays the most active role in the process of MB degradation. The ZrO$_2$ nanoparticle and ZrO$_2$ - NGP composite have good stability and reusability because the degradation efficiency does not significantly decrease after using for four cycles.

Figure 6. Reusability of (a) ZrO$_2$ and (b) ZrO$_2$ - 10 wt% NGP.

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