Improving the sonocatalytic performance of good crystallinity ZrO$_2$ nanocomposite through graphene addition

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Abstract. In this study, the catalytic performance of the ZrO$_2$ nanoparticles is enhanced by combining ultrasonic radiation with graphene material addition. The structural, morphological and surface properties of sol-gel synthesized ZrO$_2$ nanoparticles with three different annealing temperatures (350°C, 550°C, and 750°C) were investigated using various characterization methods, including X-Ray Diffraction, Transmission Electron Microscope measurements and Brunauer-Emmett-Teller measurements. The result show that if the annealing process does not take place, ZrO$_2$ nanoparticles have an amorphous structure. The formation of the crystalline structures of the tetragonal phase of the nanoparticle begins at an annealing temperature of 550°C. The highest sonocatalytic performance of nanoparticles is achieved at an annealing temperature of 550°C. The ZrO$_2$/graphene nanocomposites were produced via co-precipitation methods at all annealing temperatures. The sonocatalytic activities in the presence of ZrO$_2$/graphene nanocomposite indicate an enhancement, compared with ZrO$_2$ nanoparticles. ZrO$_2$ with and without graphene composites shows a level of stability that would allow reuse. A reasonable catalysis mechanism of ZrO$_2$ with and without graphene composites is proposed.

Keywords: ZrO$_2$, sonocatalytic, graphene, and annealing

1. Introduction

At present, the sonocatalytic process has received great attention as a useful and promising method for mineralizing organic pollutants, such as synthetic dyes, in aqueous media. In this process, water molecules are used to produce hydroxyl radicals – the primary oxidant in water purification treatment. Hydroxyl radicals are very reactive and non-selective oxidants, which are capable of decolorizing and mineralizing dyes to CO$_2$ and H$_2$O, as well as other simple inorganic products [1]. Heterogeneous sonocatalysis through ultrasonic treatment on a metal oxide semiconductor surface is an advanced oxidation process [2].

Among the various semiconductors, zirconium dioxide (ZrO$_2$) is an attractive candidate for degradation of dyes due to its interesting physical and chemical properties, low cost, high stability, and environmentally friendly status [3]. However, the degradation efficiency of ZrO$_2$ nanoparticles is not very high because of the high rate of recombination in electron-hole pairs. Therefore, the development of a new, efficient catalyst is still a major challenge.

Recently, a great deal of attention has been paid to the use of graphene materials in the catalysis field due to its large surface area [4], high rate of electronic charge transport [5], and excellent mechanical...
and chemical properties [6, 7], which make it becomes a kind of attractive adsorbent in wastewater treatment. Therefore, efforts to combine graphene with metal-oxide semiconductors have become central to the production of catalysts with high performance in the decomposition of dyes. The purpose of combining graphene with metal-oxide semiconductors is to improve degradation efficiency by increasing the charge-separation process, reducing the rate of the recombination of electron-hole pairs, and increasing the surface area of the catalyst [8].

In this study, the prepared samples were characterized via various techniques, including X-ray Diffraction (XRD), Transmission Electron Microscope (TEM) measurement, and Brunauer-Emmett-Teller (BET) measurement. The catalytic performance of ZrO$_2$ nanoparticles was enhanced by combining ultrasonic radiation with graphene material addition. Methylene blue (MB) dye was selected as a model contaminant in wastewater because MB is widely used in the dyeing and printing of textiles, and it is reasonably chemically stable and non-biodegradable. The effects of annealing temperatures, reusability, and role of reactive agents on the catalytic reaction were investigated and the results are discussed below.

2. Experimental

2.1 Materials

All the chemical reagents were of an analytical grade and were used without further purification. Zirconium(IV) chloride (ZrCl$_4$) and sodium hydroxide (NaOH) were purchased from Merck. Graphene was purchased from Angstron Materials.

2.2 Preparation of ZrO$_2$-X (with X = dry, 350, 550, or 750)

ZrO$_2$-X nanoparticles were synthesized using the sol-gel method. Briefly, ZrCl$_4$ and NaOH were dissolved separately in distilled water through magnetic stirring. Then, the ZrCl$_4$ solution was added to the NaOH solution slowly, followed by magnetic stirring for 3 h, which allowed a homogenous solution to be achieved. The temperature of solution was maintained at 80°C during the stirring process. The mixed solution was then centrifuged to separate out the products that were precipitated from the solution. The precipitates were rinsed with distilled water and ethanol several times to remove impurities. The product was heated at 120°C for 12 h. It was labeled as ZrO$_2$-dry. To raise the crystallinity up in the product, the ZrO$_2$-dry nanoparticles were calcined at various temperatures: 350°C, 550°C, and 750°C. Calcination took place in the air for 5 h, at a heating rate of 10°C min$^{-1}$. The results were labeled ZrO$_2$-350, ZrO$_2$-550, and ZrO$_2$-750, respectively.

2.3 Preparation of ZrO$_2$-X/graphene (with X = dry, 350, 550, or 750)

ZrO$_2$-X/graphene nanocomposites were synthesized using the co-precipitation method. Briefly, the graphene powder was dispersed in distilled water and an ethanol solution via ultrasonic treatment for 2 h, which was followed by the addition of the prepared ZrO$_2$-X nanoparticles into a graphene solution. The mixed solution was stirred for 1 h in order to achieve a homogeneous suspension. The suspension was then heated at 120°C for 3 h to effect deposition on to the graphene sheets. The product was collected through centrifugation and was dried in a vacuum at 70°C for 12 h in order for ZrO$_2$-X/graphene nanocomposites to be obtained.

2.4 Characterization

XRD was performed using a Rigaku Miniflex 600 diffractometer with Cu K-α radiation ($\lambda$ =1.5406 Å) in order to obtain the crystallized samples. Tecnai G2 supertwin transmission electron microscopy (TEM, accelerating = 200 kV) was used to observe particle size and the morphology of samples. The specific surface area of samples was determined using the BET method.

2.5 Sonocatalytic activity

MB was used as a model organic pollutant. The sonocatalytic activity of samples was investigated via the degradation of an MB aqueous solution with ultrasonic irradiations. Catalysts (30 mg) were dissolved in MB solution (20 mg/L). The solution kept stirred continuously in the dark condition for 30
min to ensure that an equilibrium was reached between the adsorption and desorption of MB molecules on the catalyst surface. The solution was placed in an ultrasonic bath with a fixed frequency and power of 40 kHz and 150 W, respectively. Subsequently, the solution was irradiated at regular intervals for 2 h. Every 15 min, a small amount of the water sample was collected through centrifugation so that the MB concentration could be measured with a UV-vis spectrophotometer.

2.6 Scavenger experiment. In order to determine the species involved in sonocatalytic activities, different radical scavengers were added to the solutions of MB. Ammonium oxalate, sodium sulfate, and tert-butyl alcohol (TBA) were used as scavengers for holes, electrons, and hydroxyl radical, respectively. The same measurements as described above were used.

3. Results and discussion

The XRD patterns of the as-prepared samples are shown in figure 1. The XRD spectra of tetragonal phase of ZrO$_2$-550 have four well resolved peaks at $\theta = 30.18^\circ$, 35.03$^\circ$, 50.36$^\circ$, and 59.94$^\circ$ which are indexed as reflection from [111], [200], [220], and [311] plane, respectively. However, the sample ZrO$_2$-750 has two additional diffraction peaks at $\theta = 28.13^\circ$ and 31.51$^\circ$ which attributed to the existence of monoclinic phase of ZrO$_2$, indicating that sample annealing at 750°C has mixture phases of tetragonal and monoclinic. Unlike ZrO$_2$-550 and ZrO$_2$-750, the peaks which are reflected by ZrO$_2$-350 has no sharp peak. It indicates that with annealing at 350°C the crystallized has not formed properly yet. Meanwhile, both of ZrO$_2$-dry and graphene has broad peak which indicated them are amorphous. For samples ZrO$_2$-X/graphene, the addition peak from graphene cannot be observed because amorphous structure and low content of graphene on ZrO$_2$-X/graphene that is 5 wt.% of graphene. Furthermore, no characteristic peaks from other crystalline impurities were detected by XRD, suggesting that the as-prepared samples have good purity.

The average crystallite size for ZrO$_2$-550 and ZrO$_2$-750 is calculated from Debye Scherrer’s formula (equation (1)):

$$D_{hkl} = \frac{0.89\lambda}{\beta\cos\theta}$$  \hspace{1cm} (1)

where $D_{hkl}$ is the crystallite size along the (hkl) direction, $\lambda$ is the wavelength of the X-ray, $\beta$ is the full-

![Figure 1. XRD patterns of the as-prepared samples and graphene.](image-url)
Table 1. Specific surface area of samples.

| Samples            | Specific Surface Area (m²/g) |
|--------------------|------------------------------|
| ZrO₂-350           | 286.822                      |
| ZrO₂-550           | 160.875                      |
| ZrO₂-750           | 39.069                       |
| ZrO₂-550/graphene  | 176.306                      |

Figure 2. TEM images of the as-prepared samples, (a) ZrO₂-550 and (b) ZrO₂-550/graphene.

The width half maximum of the most intense diffraction peak, and θ is the diffraction angle. The average crystallite size to be approximately 13 and 24 nm for ZrO₂-550 and ZrO₂-750, respectively. The crystallite size is related to the contact area. Reducing the crystallite-size mean increases the contact area and improves the dispersion of the samples in the solution, thus promoting interaction between photons, the catalyst, and pollutants [9-11]. Briefly, samples with a small crystallite size exhibit good catalytic performance. In other words, ZrO₂-550 should exhibit a better catalytic performance than ZrO₂-750.

The specific surface area of all the samples in the annealing process is given in table 1. It can be seen that the surface area of ZrO₂ nanoparticles decreases as the temperature increases. However, the incorporation of graphene materials enhances the surface area significantly.

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Figure 2 shows the TEM images of the pure ZrO₂-550 nanoparticles and the ZrO₂-550 nanocomposites with graphene addition. As is clear, there are agglomeration particles with a topography that is nearly spherical, indicating the presence of ZrO₂. The agglomeration probably occurred because of the high surface energy of ZrO₂ nanoparticles [12]. The aggregated structure of the ZrO₂ nanoparticles suggests a reduction in the total active surface area of the catalyst, which would have reduced catalytic performance. This might be one reason why the degradation efficiency of ZrO₂ nanoparticles was not very high.

As described earlier, the XRD measurements did not indicate the existence of graphene in ZrO₂-X/graphene nanocomposites because of its amorphous structure and low graphene content. The TEM
Figure 3. (a) Sonocatalytic activity degradation; (b) scavenger experiment for ZrO$_2$-550/graphene.

images, however, show the presence of graphene clearly. Its existence was confirmed by the presence of a layer-like structure, as seen in figure 2b. This indicates that the ZrO$_2$-X/graphene nanocomposites were synthesized successfully through the co-precipitation method.

In order to investigate the degradation kinetics of MB using the samples, the pseudo-first-order reaction model was used. The following equation was utilized as equation (2) below:

\[
\frac{C_t}{C_0} = e^{-K_{app}t}
\]  

where \(C_t\) is the concentration at any time, \(t\), \(C_0\) is the initial concentration, \(K_{app}\) is the rate constant. As figure 3a shows clearly, the degradation efficiency is increased significantly by graphene addition to ZrO$_2$-X nanoparticles. This is because of the role of graphene in increasing the charge-separation process that occurs between the MB molecules and the catalyst, which reduces the rate of the recombination of electron-hole pairs, as well as increasing the surface area of the catalyst [8]. With graphene addition, the degradation efficiency increased from 55.2% to 77.4%, 63.5% to 89.4%, 70.6% to 100%, and 75% to 100% for ZrO$_2$-dry, ZrO$_2$-350, ZrO$_2$-550, and ZrO$_2$-750, respectively. In spite of the graphene addition case, the degradation efficiency was enhanced as the annealing temperature increased. The sample that was annealed at 550°C had the best activity, when compared with the other samples. The decrease in the degradation reaction for ZrO$_2$-750 could be related to the decreasing catalyst surface area at higher temperatures, caused by aggregation and crystal growth [9-11, 13].

To ascertain the main reactive species responsible for the degradation of MB in the samples, a series of scavengers were employed. Figure 3b demonstrates the degradation of MB in the presence of selected scavengers. It can be seen that the addition of selected scavengers inhibits the sonocatalytic removal of MB in an aqueous solution. As a result, the role of the reactive species can be expressed as follows: hole > OH$^*$ > electron. Therefore, it can be concluded that holes are the main reactive species.

Stability and reusability are important issues when assessing the practical and economic implications of catalysts. In order to evaluate stability and reusability, the same catalyst was used repeatedly over four cycles. At the end of each cycle, the catalyst was separated from the MB solution via centrifuge, allowing it to be reused under the same conditions with each MB solution (as shown in figure 4). The reuse of the catalyst did not lead to any significant changes in degradation efficiency where the sonocatalytic activity was concerned, which emphasizes the good level of stability of the catalysts that were used.
Figure 4. Reusability of ZrO$_2$-550 and ZrO$_2$-550/graphene.

The sonocatalytic mechanism of pure ZrO$_2$ has been studied previously [14]. In the presence of graphene, the rate of the recombination electron-hole pairs might be inhibited due to the trapping of electrons by graphene layers. This is caused by the properties of graphene, which is a good acceptor of electrons [15].

4. Conclusions

In this study, ZrO$_2$-X nanoparticles were synthesized successfully using the sol-gel method, and ZrO$_2$-X/graphene nanocomposites were synthesized successfully using the co-precipitation method. The results were confirmed via XRD and TEM measurements. The XRD measurements showed that ZrO$_2$ nanoparticles have an amorphous structure when the annealing process has not taken place. The crystalline structures of the tetragonal phase of the nanoparticle begin to be formed at an annealing temperature of 550°C, and at 750°C, the monoclinic phase of ZrO$_2$ begins. The BET results indicated that the surface area of samples decreases as the temperature increases. Adding graphene to ZrO$_2$ significantly improved degradation efficiency. The sample that was annealed at 550°C demonstrated the best activity levels, when compared with the other samples. The scavenger experiment showed that the reactive species operates via the following sequence: hole $>$ OH$^-$ $>$ electron. In the sample, there was also a good level of stability in terms of reuse over four cycles.

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