Photocatalytic Degradation of Organic Dyes with Nanomaterials

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ABSTRACT: Zinc oxide (ZnO) nanoparticles were synthesized by reacting an aqueous-alcoholic zinc nitrate solution to sodium hydroxide under ultrasonic irradiation at room temperature. The fullerene (C60) and ZnO nanoparticles were heated individually in an electric furnace for two hours at 700 ℃. The morphology and optical properties of the C60 and ZnO nanoparticles were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and ultraviolet/visible (UV-vis) spectroscopy. The photocatalytic activity of the heated and unheated the C60 and ZnO nanoparticles for the decomposition of methylene blue (MB), methyl orange (MO) and rhodamine B (RhB) was examined using UV-vis spectroscopy.

I. Introduction

Wastewater containing residual organic dyes from the textile, paper and other industries makes serious environmental problems.1 A typical treatment of the wastewater involves either absorption or chemical coagulation. However, these methods just transfer the organic dyes from the liquid- to solid-phase, requiring further treatment and causing secondary pollution.2 The photocatalytic decomposition of organic pollutant using semiconductors, such as ZnO or TiO2 nanoparticles is a promising technology for the removal of pollutants from wastewater.3 ZnO nanoparticles have received much attention in many industry fields, such as catalysis, photochemistry, electronics and optoelectronics, owing to their semiconductor characteristics.4,6 ZnO nanoparticles show different physical and chemical properties depending on the morphology of the nanostructure.6 The sizes and shapes of ZnO nanoparticles considerably depending on the preparation method, so, ZnO nanoparticles has various morphology such as spherical, quasi spherical, rods, wires, needles, and flower-like. ZnO nanoparticles are used as a photocatalyst to reduce the level of environmental pollutants because its photocatalytic degradation mechanism is similar to that of TiO2.7-10 Since photocatalytic process is based on the generation of electron/hole pairs by band-gap radiation, the coupling of different nanomaterials appears to be useful for achieving more efficient electron/hole pair separation under ultraviolet irradiation.10-12 C60 has attracted interest owing to its special electronic properties.13 One of the most remarkable properties of C60 is its ability to dimerize in the electron-transfer process is that it can efficiently excite rapid photoinduced charge separation and a relatively slow charge recombination.14 Accordingly, a combination of photocatalyst and C60 can provide an ideal system for achieving enhanced charge separation by photoinduced electron transfer. Some of the C60 complexes have shown promising photovoltaic effects in photo-irradiation.15-17 Therefore, an attempt was made to increase the photodegradation efficiency of ZnO nanoparticles and C60 as a catalyst. In this study, C60 and ZnO nanoparticles were evaluated as a catalyst in the photocatalytic degradation
of organic dyes using UV-vis spectroscopy. The photocatalytic activity of the heated and unheated C60 and ZnO nanoparticles for the decomposition of MB, MO and RhB were examined. The application field of this study will be used in materials science such as photocatalyst and additives in nanocomposite.

II. Experimental

1. Chemicals and instruments

Zn(NO3)2 · 6H2O, NaOH, and ethanol were purchased from Samchun Chemicals. Fullerene[C60] was supplied by Tokyo Chemical Industry Co., LTD. The crystalline structures were characterized by X-ray diffraction (XRD, Rigaku DMAX PSPC MDG 2000). The morphology of nanoparticle was observed with scanning electron microscopy (SEM, Hitachi S4700) at an accelerating voltage between 0.5 and 30 kV and TEM (JEOL Ltd, JEM-2010) at an accelerating voltage of 200 kV. The ultraviolet/visible (UV-vis) spectra were recorded with a Shimazu UV - 1601PC spectrometer. Ultrasonic irradiation of all samples was carried out in continuous mode with an ultrasonic generator UGI1200 (Hanil Ultrasonic Co., Ltd.) with a frequency of 20 kHz and normal power of 750 W. The configuration of the equipment of ultrasonic generator was a horn type system with a horn tip diameter of 13 mm. An electric furnace (Ajeon Heating Industry Co., Ltd.) was used to heat the C60 and ZnO nanoparticles. A UV lamp (8 W, 254 nm, 77202 Marne La Valee-cedex 1 France) was used as the source of the ultraviolet light irradiation.

2. Preparation of ZnO nanoparticles and C60 as a photocatalyst

In typical experiments, 1.0 M Zn(NO3)2 · 6H2O and 10 M NaOH were dissolved in 6 ml of distilled water. 15 ml of ethanol was added to each solution. After combining two solutions in a beaker, the solution was reacted under ultrasonic irradiation for 45 min at room temperature. At the end of the reaction, the above solution was removed and the white precipitates at the bottom of the beaker were washed with distilled water and ethanol, and dried at room temperature.18 The C60 and ZnO nanoparticles were heated in an electric furnace in argon gas for 2 hours, and then cooled to room temperature over 4 hours.

3. Evaluation of photocatalytic activity of C60 and ZnO nanoparticles

The unheated ZnO nanoparticles and C60, heated ZnO nanoparticles and C60 were used as catalysts to evaluate their effects for the degradation of organic dyes. 10 mg of each catalyst such as the unheated ZnO nanoparticles, C60, heated ZnO nanoparticles and C60 was put into a 10 ml vial containing 10 ml of each aqueous solution 0.01 mM of MB, MO and RhB. The vial was irradiated for one hour with a wavelength of 254 nm using a UV-lamp. The degradation of the organic dyes by the nanomaterial photocatalysts was investigated using UV-vis spectroscopy.

III. Results and discussion

ZnO nanoparticles were prepared with Zn(NO3)2 · 6H2O and NaOH in aqueous-alcoholic solution under ultrasonic irradiation. The crystallinity of the heated and unheated nanomaterials such as ZnO and C60 was examined by XRD.18,19 Figure 1 presents the XRD patterns of (a) unheated C60 and (b) heated C60 in an electric furnace at 700 °C in Ar for two hours. Figure 1 demonstrates that the intensity of (311) peak decreases from 1800 to 1300 a.u. after the heat treatment, owing to the high temperature affected the structure of C60. Figure 2 presents the XRD patterns of (a) unheated ZnO nanoparticles and (b) heated ZnO nanoparticles. The (100)

![Figure 1](image1.png)  
*Figure 1. The XRD patterns of (a) unheated C60 and (b) heated C60 in an electric furnace at 700 °C in Ar for 2 hours.*
XRD peak showed a significant increase in intensity, whereas the (002) peak showed also increase due to high temperature affected the structure of ZnO nanoparticles. This means that crystal orientation of the ZnO nanoparticles was changed by heating.

Figure 3 shows SEM images of (a) unheated and (b) heated C_{60}. The shape of C_{60} was changed by heating in an electric furnace. The unheated structure of C_{60} was broken down into small particles but the structure of the heated C_{60} had broken into nanosized pieces, which resulted in some increased surface area which could be reacted with organic dyes as a catalyst.

Figure 4 presents SEM images of (a) unheated and (b) heated ZnO nanoparticles. There was some difference in the morphology of the unheated and heated ZnO nanoparticles. The morphologies of the unheated and heated ZnO nanoparticles were needle like types and quasi sphere like types, respectively. As the size of the ZnO nanostructures depends on the heating temperature, the higher heating temperature results in increased particle size of ZnO nanoparticles.

Figure 5 represents TEM images of (a) original C_{60} and (b) heated C_{60}. Most of structure of original C_{60} was shown layered shape in Figure 5(a). In Figure 5(b), it presented the fragmented shape of original C_{60}. The structure of original C_{60} was altered to small pieces by electric furnace at 700 °C under Ar gas for 2 hours. The results of TEM images mean that the structure of original C_{60} was broken by high temperature and increased their surfaces by changing structure due to forming of fragmentation.

The TEM images of (a) unheated ZnO nanoparticles and (b) heated ZnO nanoparticles in an electric furnace at 700 °C in Ar gas for 2 hours were presented in Figure 6. The structure of unheated ZnO nanoparticles in Figure 6(a) had various shapes like a trigonal, hexagonal, spherical and porous form.
Figure 4. SEM images of (a) unheated ZnO nanoparticles and (b) heated ZnO nanoparticles in an electric furnace at 700 °C in Ar gas for 2 hours.

Figure 5. TEM images of (a) original C$_{60}$ and (b) heated C$_{60}$ in an electric furnace at 700 °C under Ar gas for 2 hours.

Figure 6. TEM images of (a) unheated ZnO nanoparticles and (b) heated ZnO nanoparticles in an electric furnace at 700 °C in Ar gas for 2 hours.
Figure 7. Plot $\ln[X]$ versus time for the degradation of the organic dye solutions using UV-vis spectroscopy with (a)-(c) of unheated C$_{60}$ and (d)-(f) of heated C$_{60}$ as a catalyst under ultraviolet light.

Figure 8. Plot $\ln[X]$ versus time for the degradation of the organic dye solutions using UV-vis spectroscopy with (a)-(c) of unheated ZnO nanoparticles and (d)-(f) of heated ZnO nanoparticles as a catalyst under ultraviolet light.

Figure 6(b) showed structure changes of unheated ZnO nanoparticles. The surface of unheated ZnO nanoparticles was altered well-round form by using electric furnace at 700 °C in Ar gas for 2 hours. Also, heated ZnO nanoparticles appeared porous and good agglomeration.

The photocatalytic degradation of MB, MO, and RhB in aqueous solution containing the photocatalysts was examined using UV-vis spectroscopy under ultraviolet light irradiation at 254 nm. To confirm the photocatalytic activity of the nanomaterials with organic dyes which were mentioned above, we compared with and without the photocatalysts such as C$_{60}$, ZnO using UV-vis spectroscopy. Figure 7 and 8 show the degradation of the organic dyes using the nanomaterials under the ultraviolet irradiation for 6 hours by UV-vis spectroscopy. The Figure 7 displayed the plot $\ln[X]$ (degradation rate constant) versus time for the degradation of the organic dye solutions using (a)-(c) the unheated C$_{60}$ and (d)-(f) heated C$_{60}$ as a catalyst under ultraviolet light. In Figure 7, photocatalytic effect for the degradation of the organic dyes such as MB, MO, RhB using C$_{60}$, in orders of following things are (e) > (d) > (f) > (a) ≈ (b) ≈ (c).

The photodegradation of the dyes with the ZnO photocatalyst has been reported.\textsuperscript{22,24} Figure 8 shows that the degradation rate constant ($\ln[X]$) of MB, MO, RhB using the unheated and heated ZnO nanoparticles. The organic dye solutions containing the unheated and heated ZnO nanoparticles were exposed to ultraviolet light at 254 nm for 6 hours. The concentration of the organic dye solutions was monitored using UV-vis spectroscopy by 6 times per an hour. In Figure 8, photocatalytic effect for the degradation of the organic dyes such as MB, MO, RhB using ZnO nanoparticles in orders of following things are (d) > (e) ≈ (f) > (a) ≈ (b) ≈ (c). The heated ZnO nanoparticles reduced the concentration of the organic dye solutions faster than the unheated ZnO nanoparticles. This phenomenon was caused by the altered structure of the ZnO nanoparticles at high temperature. The decrease in the number of surface active sites was caused by the change in shape of ZnO nanoparticles from needle-like to quasi-sphere at high temperatures. The photocatalytic effect was increased due to the aggregation of ZnO nanoparticles at high concentration.\textsuperscript{24}

IV. Conclusions

The photocatalytic activity of the heated and unheated the C$_{60}$ and ZnO nanoparticles for the degradation of MB, MO, and RhB was examined using UV-vis spectroscopy. XRD data showed that the structures of the nanomaterials had been transformed by heating in an electric furnace at 700 °C for 2 hours. SEM data revealed some change on the morphology of C$_{60}$ and ZnO nanoparticles after heating 700 °C for 2 hours. From the TEM images of unheated C$_{60}$ and heated C$_{60}$, the structure of unheated C$_{60}$ was fragmentized by heating in an electric furnace at 700 °C for 2 hours. Also, the TEM images of unheated ZnO nanoparticles and heated ZnO nanoparticles showed the shape changed from various shape such as trigonal, hexagonal, spherical and porous ZnO nanoparticles at 25 °C to agglomerated ZnO particles at 700 °C. The heated nanomaterials were more effective in the photocatalytic degradation of the organic dyes than the unheated nanomaterials. The most effective photocatalyst for the degradation of the organic dyes such as MB, MO, RhB by using C$_{60}$, is the heated C$_{60}$ for the degradation of RhB. In case of ZnO as a photocatalyst, the heated ZnO nanoparticles are the most effective for the degradation of MB.

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