Enhancement of Photocatalytic Activity of Synthesized ZnO Nanoparticles with Oxygen Plasma Treatment

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Abstract

ZnO nanoparticles were synthesized by the spray-pyrolysis method. They were exposed to oxygen plasma treatment to increase OH radicals on their surfaces. ZnO nanoparticles were spherical grains with a narrow size range of about 7~10 nm, and these small particles agglomerated together to form larger clusters. Synthesized ZnO nanoparticles and a p-25 mixed MB solution exposed to UV illustrate that p-25 has a better photo-degradation response than synthesized ZnO nanoparticles using UV light. Therefore, we did oxygen plasma treatment to increase OH radicals on the surface of synthesized ZnO nanoparticles. As a result, the photocatalytic activity of oxygen plasma treated ZnO nanoparticles was enhanced by about 60% based on the absorption peak of the decomposed MB solution. Also, we have analyzed the surface of oxygen plasma treated ZnO nanoparticles by XPS. Results showed that OH radicals and molecular water on the ZnO surface are enhanced by oxygen plasma treatment. Also, treatment reduced oxygen and zinc vacancies on the treated ZnO surface.

Keywords: ZnO; Oxygen Plasma; OH radical; Photocatalyst; X-ray Photoelectron Spectroscopy

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1. Introduction

In the past few decades, oxide semiconductors have been well known as photocatalysts [1-3] since the Honda-Fujishima effect [4, 5] was reported in the 1970s. They reported a photocatalytic effect in TiO_2 wherein water split on the TiO_2 electrode. Since then, much research in photocatalysis has been performed with semiconductor oxide materials such as TiO_2 , ZrO_2 , SnO_2 and ZnO [1, 6, 7]. Zinc oxide is a direct band gap (3.37 eV) semiconductor, which has a hexagonal wurtzite structure. ZnO is a good candidate for photocatalysis because it has physical and chemical stability, high oxidative properties, and absorbs ultraviolet light. When ZnO is irradiated by UV light, redox (reduction and oxidation) reactions will occur on the ZnO surface, generating O_2^- and OH radicals. These two powerful oxidizing agents have been proven to be effective in the degradation of harmful organic materials, converting them into CO_2 and H_2O . Therefore, we assume that the presence of oxygen on the surface of ZnO is a very important factor in the photocatalytic activity of ZnO nanoparticles. Hydroxyl radicals attack the C-H bonds of organic compounds to lead to complete mineralization. The effective separation of electron-hole pairs or the enhanced degradation of organic pollutants can be realized by increasing the concentration of electron donors such as surface hydroxyl groups and by the enhanced reduction of adsorbed molecular oxygen. An increase in the concentration of surface hydroxyl groups may be achieved by the addition of foreign metal oxide [8-10]. According to S. K. Lam [11], thermal treatment in air allows more oxygen molecules to be adsorbed on the surface of TiO_2 . These oxygen molecules act as photoexcited electron traps and inhibit the recombination of photoexcited electrons and holes.

In this study, ZnO nanoparticles were synthesized by the spray-pyrolysis method and were O_2 plasma surface treated to increase O_2^- or OH radicals on the surface. We studied the photocatalytic activity of synthesized ZnO nanoparticles as compared with commercial TiO_2 powder (Degussa P-25). Synthesized ZnO nanoparticles were characterized by scanning

electron microscopy (SEM), transmittance electron microscopy (TEM), energy dispersive spectrometry (EDS), X-ray diffraction (XRD) and Brunauer-Emmett-Teller (BET) tests. The photocatalytic activity of synthesized-ZnO nanoparticles was evaluated using UV-VIS absorption spectroscopy through degradation of a Methylene Blue (MB) solution. We used X-ray photoelectron spectroscopy (XPS) to assess the difference before and after O₂ plasma surface treatment.

2. Experimental details

ZnO nanoparticles were synthesized by spray-pyrolysis. A homemade spray-pyrolysis system composed of a furnace, sonication system and temperature controller was used. The synthesis solution was prepared by mixing zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) with distilled water to a concentration of 0.5M, followed by stirring for 30 min. This solution was used as the precursor in the synthesis of ZnO nanoparticles. [The solution was sprayed by sonication and flow into a vertical quartz reactor in a furnace at 800 °C and 900 °C without carrier gas.](#) The synthesis temperature was maintained for 60 min. Crystal structure was identified by an X-ray diffractometer with Cu K α_1 radiation. O₂ plasma surface treatment was applied to the synthesized ZnO nanoparticles using a microwave plasma treatment system at a frequency of 2.45 GHz. ZnO nanoparticles were exposed to flowing oxygen gas at a power of 300 W for 300 sec in the microwave plasma system. The working pressure was 250 mTorr, and the O₂ flux was changed from 20 sccm to 100 sccm in 20 sccm intervals, as noted in Table 1.

A Methylene Blue (MB, C₁₆H₁₈ClN₃S) solution was prepared by dissolving 0.008 g of MB in 1000 mL distilled water, for a concentration of 2.50×10^{-5} M (mole/L). This MB solution was used as a test for the photocatalytic activity of synthesized ZnO nanoparticles and commercial TiO₂ powder (P-25). Prepared ZnO nanoparticles (1 mg) were placed in a 1 cm × 1 cm plastic cuvette and filled with 5 mL of MB solution. The cuvette was irradiated by UV

light (254 nm) in a black box. Photo-degradation was monitored over time using UV-VIS spectroscopy. Specifically, absorption spectra of the degradation of MB in solution were measured at intervals of 10 min for an hour.

3. Results and Discussion

Figure 1 shows the SEM images and EDS data which were synthesized ZnO nanoparticles via spray-pyrolysis method at 800 and 900 °C for 60 min, respectively. We used EDS (Energy Dispersive Spectrometry) to confirm the difference of element ratio of ZnO nanoparticles. Zn:O atomic% ratio of synthesized ZnO nanoparticles was about 1:1. Synthesized ZnO nanoparticles at 800 °C were had a little more zinc as compared with synthesized ZnO nanoparticles at 900 °C. Element ratio of synthesized ZnO nanoparticles at temperature over 800 °C did not influenced synthesis temperature.

Figure 2 and Table 2 provide physical-chemical properties of synthesized ZnO nanoparticles. Figure 2(a) shows SEM and TEM images of ZnO nanoparticle synthesized at 900 °C for 60 min by spray-pyrolysis. Synthesized ZnO nanoparticles were approximately 1 µm in size and had the shape of crumpled paper. Spray-pyrolysis synthesized materials have fast synthesis rates at high temperature, resulting in the irregular shapes. Synthesized ZnO nanoparticles were spherical grains with a narrow size range of about 7~10 nm based on high resolution TEM images. Also, these small particles were agglomerated together to form larger clusters. Figure 2(b) shows XRD patterns of ZnO nanoparticles synthesized at 900 °C for 60 min. The d-spacing values and relative intensities of the peaks coincide exactly with the JCPDS data for pure ZnO, which crystallizes in a hexagonal wurtzite structure. These particles consist of polycrystalline grains and preferential growth was observed. Thus, the spray-pyrolysis synthesis yielded pure ZnO nanoparticles that have no impurities.

Table 2 provides the mean size of ZnO nanoparticles synthesized at 900 °C based on XRD

and TEM image data. Also, the surface area of synthesized ZnO nanoparticles was defined through the Brunauer-Emmett-Teller (BET) method using N₂ adsorption at 77 K. The average size of the ZnO nanoparticles was calculated from the full width at half maximum (FWHM) of the highest intensity peak, (101), according to the Scherrer equation, $t = k \cdot \lambda / B \cdot \cos\theta$, where k is a constant taken as 0.9, λ is the wavelength of the X-ray radiation ($\lambda = 0.154$ nm), θ is the diffraction angle and B is the FWHM of the XRD peak. The average size of the ZnO nanoparticles was 17.5 nm, based on the Scherrer equation. Thus, particle size calculated from XRD was 10 nm higher than that observed from the TEM image. Based on this, the size of the particle domains and the actual particle size were not the same.

Figure 3 shows the surface areas of ZnO nanoparticles before and after oxygen plasma treatment irradiation. Before oxygen plasma irradiation, ZnO nanoparticles had 44 m²/g of surface areas and 0.12 ml/g of total volume. Also, ZnO nanoparticles had 43 m²/g of surface areas and 0.18 ml/g of total volume after oxygen plasma irradiation. This result means that oxygen plasma treatment was influenced change of surface functional group but was not change the surface areas.

The photocatalytic activity of synthesized ZnO nanoparticles was carried out using UV light. A Methylene Blue (MB) solution was used as a test contaminant since it has been extensively used as an indicator for photocatalytic activities owing to its absorption peaks in the visible range. Figure 4 shows photo-degradation experimental results for MB with synthesized ZnO nanoparticles, TiO₂ (p-25, Degussa), and O₂ treated ZnO nanoparticle under UV irradiation. The first curve (squares) represents only MB dissolved in water and shows very small degradation (6.8 %) when irradiated with UV light. This smaller degradation of MB might be due to the interaction of MB with OH radicals in water. The second curve (circles) corresponds to the MB solution mixed with synthesized ZnO nanoparticles, while the third curve (triangles) is the p-25/MB solution. As shown, p-25 has better photo-degradation

response than synthesized ZnO nanoparticles using UV light. Photocatalytic activity of ZnO is attributed to both the donor and acceptor states caused by the large number of defect sites from oxygen or zinc vacancies [12]. However, lower photo-degradation of MB with UV and synthesized ZnO nanoparticles may be caused by a small amount of oxygen or zinc vacancies. We presume that this lower photo-degradation may be due to the faster recombination of electron-hole pairs or a decrease in OH radical. Therefore, oxygen plasma treatment was performed to increase OH radicals on the synthesized ZnO nanoparticle surface, as shown in Table 1.

Plasma surface treatment has been investigated by many researchers for the purpose of modifying surfaces [13, 14]. Microwave surface O₂ plasma treatment was used to introduce oxygen into the surface of synthesized ZnO nanoparticles. The O₂ gas flux was increased gradually in increments of 20 sccm from 20 sccm up to 100 sccm. After that, the absorption spectrum of the MB solution with the O₂ plasma treated-ZnO nanoparticles was measured by UV-Vis spectroscopy. The photocatalytic activity of synthesized ZnO nanoparticles was enhanced for O₂ plasma treated samples. The photo-degradation rate of MB with O₂ treated ZnO nanoparticles irradiated with UV light was much faster than non-treated ZnO nanoparticles irradiated with UV light, as shown in Figure 4. It took only 15 min for O₂ treated ZnO to decolorize 50 % of the MB while, for non-treated ZnO, it took more than 40 min. This faster degradation rate of MB is attributed to increased OH radicals. Also, we assume that faster photo-degradation effects may be due to decreased recombination of electron-hole pairs.

We were checking the change of O-H stretching peak after photocatalytic reaction via FT-IR spectrum in figure 5. O-H stretching peak was increased on the ZnO nanoparticles surface by oxygen plasma treatment. Also, O-H stretching peak has decreased after photocatalytic reaction. This trend is similar to the photocatalytic efficiency.

We had researched ZnO and TiO₂ nanoparticles before/after oxygen plasma treatment for improvement of photocatalytic activity in figure 6. After oxygen plasma treatment, ZnO and TiO₂ nanoparticles had photocatalytic activity enhancement. However, TiO₂ nanoparticles had not maintained improved photocatalytic activity at repeated reaction. By comparison, oxygen treated ZnO nanoparticles maintained the improved photocatalytic activity. This is a very important point and because of this, we used a ZnO material.

We examined photocatalytic activity of ZnO nanoparticles in repeated reactions. Figure 7 shows the photocatalytic activity of oxygen plasma treated ZnO nanoparticles in repeated reactions. Photocatalytic activity of oxygen plasma treated ZnO nanoparticles steadily decreased over the 10 times of recurrent reaction. The initial photocatalytic efficiency is decreased by approximately 8% and the final photocatalytic efficiency was reduced by about 10%. This result means that photocatalytic activity was maintained consistently for reabsorption of –OH radical and molecular water in methyleneblue solution.

Figure 8 show that EPR (Electron Paramagnetic Resonance) spectrum confirmed the correlation between changes in photocatalytic activity and changes in O₂^{•-} (superoxide) groups after water treatment. The g factor was calculated via: $\Delta E = h\nu = g \cdot \mu_B \cdot B_0$, where h is the Planck constant, ν the microwave frequency, g the g factor, μ_B the Bohr magneton, and B_0 the magnetic field, respectively. For EPR measurements, the microwave frequency was 9.648 GHz. Thus, the calculated g factor was 1.96 for samples with O₂^{•-}(superoxide). In Figure 8, before/after oxygen plasma treated ZnO nanoparticles had a g factor of 1.96 with O₂^{•-} (superoxide). However, the intensity of the EPR spectrum did not change, indicating that O₂^{•-} is not an important factor in photocatalytic activity.

We used X-ray electron spectroscopy (XPS) to assess the difference before and after the O₂ plasma surface treatment. The core level of Zn 2p spectra shows similar features in both the untreated and oxygen treated ZnO nanoparticles. Figure 9(a) shows the XPS data of Zn 2p in

synthesized ZnO nanoparticles before and after O₂ plasma treatment. On the surface, Zn 2p core level peaks were shifted to a high binding energy region from 1022.6 eV to 1023.1 eV. This result means that synthesized ZnO nanoparticles change from ZnO containing metallic zinc to more oxygen-rich zinc. Figure 9(b) shows the O 1s spectra of synthesized ZnO nanoparticles before and after O₂ plasma treatment. The broad shoulder at the higher binding energy side of the main O 1s peak of ZnO nanoparticles before O₂ treatment can be fitted with two peaks at 533.1 and 534.1 eV, respectively. These two peaks match the physically absorbed OH radical at 533.1 eV and molecular water at 534.1 eV. According to the results of thermal desorption spectroscopy (TDS) by Zwicher and Jacobi [15], the adsorption of molecular water on ZnO is quite complex. The shoulder peak increased noticeably and intensity increased in fitted peaks, indicating that both the chemisorption and physisorption of OH radicals and molecular water on the ZnO surface are enhanced by O₂ plasma treatment. Figure 9(c) shows the XP spectra of O 1s peak in the range of 530 to 537 eV. Oxygen plasma treatment process was increased peaks that are formed from OH radical and molecular water at the same time. The oxygen plasma treatment has affected not only increasing of OH radical, but ZnO surface adsorption of molecular water in the air as well. Also, OH radicals and molecular water groups decomposed the MB solution by cracking double bonds (C=N, C=S), and coupling with the N-H single bond of the MB solution.

4. Conclusion

In this study, ZnO nanoparticles were synthesized by the spray-pyrolysis method at 900 °C for 60 min and were exposed to O₂ plasma treatment to increase OH radicals on their surfaces. Synthesized ZnO nanoparticles were spherical grains with a narrow size range of about 7~10 nm, and these small particles agglomerated together to form larger clusters. Synthesized ZnO nanoparticles and a p-25 mixed MB solution exposed to UV illustrate that p-25 has a better

photo-degradation response than synthesized ZnO nanoparticles using UV light. Therefore, we did oxygen plasma treatment to increase OH radicals on the surface of synthesized ZnO nanoparticles. As a result, the photocatalytic activity of O₂ plasma treated ZnO nanoparticles was enhanced by about 60 % based on the absorption peak of the decomposed MB solution. Also, we have analyzed the surface of O₂ plasma treated ZnO nanoparticles by XPS. Results showed that OH radicals and molecular water on the ZnO surface are enhanced by O₂ plasma treatment. Also, treatment reduced oxygen and zinc vacancies on the treated ZnO surface.

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Figure captions

Figure 1. SEM images and EDS data were synthesized ZnO nanoparticles at 800 and 900 °C for 60 min via spray-pyrolysis method.

Figure 2. (a) SEM surface morphology and high resolution TEM image of ZnO nanoparticles synthesized at 900 °C for 60 min by spray-pyrolysis and (b) XRD patterns of synthesized ZnO nanoparticles.

Figure 3. Surface areas of ZnO nanoparticles before/after oxygen plasma treatment irradiation.

Figure 4. Photoreduction of MB with respect to time using the MB only solution, synthesized ZnO, TiO₂ powder (Degussa, p-25) and oxygen plasma treated ZnO exposed to UV light.

Figure 5. (a) FT-IR high resolution spectrum of O-H stretching peak before/after photocatalytic reaction.

Figure 6. Photocatalytic activity test of ZnO and TiO₂ nanoparticles in repeated reaction.

Figure 7. Photocatalytic activity of oxygen plasma treated ZnO nanoparticles in 10 time s of repeated reactions.

Figure 8. EPR spectrum of ZnO nanoparticles; (a) untreated, (b) oxygen plasma treated.

Figure 9. Changes in XPS spectra of ZnO in the (a) Zn 2p, (b) O 1s peak and (c) OH and H₂O peaks in O 1s regions before and after O₂ plasma treatment.

Table captions

Table I. Oxygen plasma treatment conditions for the surface modification of synthesized ZnO nanoparticles by microwave plasma system.

O₂ plasma treatment conditions				
Microwave frequency	O₂ flux	Power	Treatment time	Working pressure
2.45 GHz	20~100 sccm	300 W	300 sec	250 mTorr

Table II. Particle size by XRD, TEM data and surface area of synthesized ZnO nanoparticles at 900 °C for 60 min.

Syn. Temp.	Particle size by XRD data (PS-1)	Particle size by TEM data (PS-2)	Surface area
900 °C	17.5 nm	8.5 nm	43 m²/g

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Graphical Abstract

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