INTRODUCTION

Lately, synthesis methods of fullerene (C$_{60}$) nanowhiskers have gathered much attention because of their potential application in diverse fields of materials chemistry. Fundamentally, the synthesis of fullerene nanowhiskers formed by individual fullerene molecules have attracted much attention in different fields including solar cells, batteries, fuel cells, sensors, catalysis etc., because of their particular structure and morphology. The fullerene nanowhiskers (or carbon nanofiber; C$_{60}$NWs) were synthesized by the liquid-liquid interfacial precipitation (LLIP) method as the derivatives of fullerene. The crystals of fullerene nanowhiskers showed needlelike crystals with a size distribution from sub-micrometers to several hundred micrometers.

The applications of zinc oxide nanoparticles were photocatalysis, composite materials, sensors and dye-sensitized solar cells owing to their outstanding optical, electrical, mechanical and chemical characters. The physical and chemical characters of ZnO nanoparticles can be controlled by handling their microstructures to perform the requirements of specific applications. Owing to the many applications of ZnO nanoparticles in chemistry, preparation of ZnO nanoparticles has been used to several methods including gas-phase reactions, hydrothermal synthesis, wet chemical synthesis, sol-gel and evaporative decomposition of the solution.

EXPERIMENTAL

Fullerene nanowhisker nanoparticles were supplied from National Institute for Materials Science, Japan. Zn(NO$_3$)$_2$·6H$_2$O, NaOH, tetrahydrofuran and ethanol were obtained from Samchun Chemicals. Organic dye (methylene blue) was supplied by Sigma-Aldrich.

An electric furnace (Ajeon Heating Industry Co., Ltd.) was used to heat the sample. An UV lamp (8 W, 254 nm, 77202...
Marne La Valee-cedex 1 France) was used as the ultraviolet light irradiation source.

The surfaces of unheated FNW-ZnO nanocomposites and heated FNW-ZnO nanocomposites were observed by scanning electron microscopy (SEM, Hitachi S4700) at an accelerating voltage of 0.5-15 kV. The morphology and crystallite size of the samples were examined by transmission electron microscopy (TEM, JEOL Ltd, JEM-2010) at an acceleration voltage of 200 kV. The structures of the nanomaterials were examined by X-ray diffraction (XRD, Bruker, D8 Advance, Germany) with CuKα target and secondary monochromator, V = 40 kV, A = 40 mA, Ni filter. Ultraviolet-visible (UV-VIS) spectroscopy of the samples was performed using an UV-VIS spectrophotometer (Shimazu UV-1601PC). All samples were treated under continuous conditions by ultrasonic irradiation using an ultrasonic generator UGI1200 (Hanil Ultrasonic Co., Ltd.) with a frequency 20 kHz and a normal power of 750 W. The ultrasonic generator was a horn type system with a horn tip diameter of 13 mm.

Synthesis of ZnO nanoparticles: In a typical experiment, 1 M of Zn(NO₃)₂·H₂O and 10 M of NaOH were dissolved in 6 mL of distilled water. Subsequently, 15 mL of ethanol was added to each solution. After mixing two solutions in a beaker, the resulting solution was placed under ultrasonic irradiation for 45 min at room temperature. At the end of the reaction, the above solution was removed and the white precipitate at the bottom of the beaker was washed with distilled water and ethanol and dried at room temperature[16,30,31].

Synthesis of FNW-ZnO nanocomposites: In a typical experiment, the prepared FNW and prepared ZnO nanoparticles were mixed at a mass ratio of 1:1. The mixture was dissolved in 10 mL of THF (tetrahydrofuran) with constant stirring to produce the FNW-ZnO nanocomposites. The mixture was then dried at room temperature. After drying, the nanocomposites were heated in an electric furnace at 700 °C for 2 h.

Degradation of organic dye with nanocomposites: The photocatalytic activity of unheated FNW-ZnO nanocomposites and heated FNW-ZnO nanocomposites were examined using methylene blue solution. 10 mg of each nanomaterial was dispersed in 10 mL of water containing 0.01 mM of methylene blue solution. All the mixture solutions were irradiated with ultraviolet light at 254 nm. The methylene blue solution was degraded by each nanomaterial under ultraviolet light was characterized by UV-visible spectrophotometer.

RESULTS AND DISCUSSION

Fig. 1(a-b) showed SEM images of unheated FNW-ZnO nanocomposites and heated FNW-ZnO nanocomposites, respectively. The ZnO nanoparticles in both unheated FNW-ZnO nanocomposites and heated FNW-ZnO nanocomposites were located above the FNW nanoparticles. Also, the particle size of the unheated FNW-ZnO nanocomposites was larger than that of the heated FNW-ZnO nanocomposites.

Fig. 2 showed TEM images of unheated FNW-ZnO nanocomposites and heated FNW-ZnO nanocomposites. The FNW nanoparticles in the heated FNW-ZnO nanocomposites were broken into smaller particles compared to the unheated FNW-ZnO nanocomposites. Therefore, unheated FNW nanoparticles in unheated FNW-ZnO nanocomposites showed more crystallinity than heated FNW nanoparticles in heated FNW-ZnO nanocomposites. As a consequence, heated FNW-ZnO nanocomposites had higher surface area than unheated FNW-ZnO nanocomposites. Also, the shape of ZnO nanoparticles in heated FNW-ZnO nanocomposites was changed rod type to plate like type. As a result, heated FNW-ZnO nanocomposites showed a more pronounced photocatalytic effect in the degradation of methylene blue than unheated FNW-ZnO nanocomposites.

Fig. 3 showed XRD patterns of unheated FNW-ZnO nanocomposites and heated FNW-ZnO nanocomposites. Both unheated FNW-ZnO nanocomposites and heated FNW-ZnO nanocomposites showed similar XRD patterns. The ZnO nanoparticles peaks of unheated FNW-ZnO nanocomposites were observed at ca. 31.71, 34.38, 36.23, 47.53, 56.60, 62.83, 66.38, 67.90, 69.01, 72.58 and 76.90° as a 2θ value. Also, the ZnO nanoparticles peaks of heated FNW-ZnO nanocomposites were observed at ca. 31.61, 34.34, 36.15, 47.39, 56.50, 62.76, 66.21, 67.86, 68.95, 72.64 and 76.80° as a 2θ value. In addition, the FNW nanoparticles peaks of heated FNW-ZnO nanocomposites were observed at approximately 10.59, 15.7 and 20.57° as a 2θ value as shown in Fig. 3(a). Whereas the ZnO nanoparticles peaks of heated FNW-ZnO nanocomposites were observed at ca. 31.61, 34.34, 36.15, 47.39, 56.50, 62.76, 66.21, 67.86, 68.95, 72.64 and 76.80° as a 2θ value.
20.47° as a 2θ value as shown in Fig. 3(b). After heat treatment, the XRD patterns of heated FNW-ZnO nanocomposites showed lower intensity than the XRD patterns of unheated FNW-ZnO nanocomposites. As a consequence, unheated FNW-ZnO nanocomposites had more crystallinity than heated FNW-ZnO nanocomposites.

Fig. 4(a-b) showed UV-visible spectra of the degraded methylene blue solution with unheated FNW-ZnO nanocomposites and heated FNW-ZnO nanocomposites under ultraviolet irradiation at 254 nm. Because of the heat treatment, the FNW nanoparticles in the heated FNW-ZnO nanocomposites were broken smaller particle size. Also, the FNW nanoparticles in the heated FNW-ZnO nanocomposites had a porous surface. So, the heated FNW-ZnO nanocomposites had more wide surface area than the unheated FNW-ZnO nanocomposites. The smaller particle size, porous surface and more wide surface area were important to improve photocatalytic degradation. As a result, heated FNW-ZnO nanocomposites showed more effective degradation of methylene blue solution than unheated FNW-ZnO nanocomposites.

**Conclusion**

Unheated FNW-ZnO nanocomposites and heated FNW-ZnO nanocomposites were synthesized as a photocatalyst for the degradation of methylene blue solution under ultraviolet irradiation at 254 nm. Unheated FNW-ZnO nanocomposites and heated FNW-ZnO nanocomposites showed similar
morphologies but the heated FNW-ZnO nanocomposites had smaller particle size than the unheated FNW-ZnO nanocomposites. The ZnO nanoparticles in the heated FNW-ZnO nanocomposites were transformed from rod type to plate like type after heating at 700 °C for 2 h. The heated FNW-ZnO nanocomposites had larger surface area and porous surface due to the high temperature heat treatment. Therefore, heated FNW-ZnO nanocomposites were more effective in degrading the methylene blue solution. Overall, heated FNW-ZnO nanocomposites had better photocatalytic effect in the degradation of methylene blue solution under ultraviolet irradiation at 254 nm than unheated FNW-ZnO nanocomposites.

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REFERENCES