Preparation of C60 Nanowhiskers/WO3 Nanocomposites and Photocatalytic Degradation of Organic Dyes

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Abstract: C60 nanowhiskers were synthesized from C60 by liquid-liquid interfacial precipitation (LLIP) using C60-saturated toluene and isopropyl alcohol. The WO3 nanoparticles were synthesized by adding 3.8 × 10−4 mole amount of ammonium metatungstate hydrate (H26N6O40W12·H2O) to 500 ml of distilled water, and the resulting solution was heated on a hot plate for 4 h. The C60 nanowhiskers/WO3 nanocomposites were prepared with C60 nanowhiskers and WO3 nanoparticles in an electric furnace at 700°C in an argon gas atmosphere for 2 h. The C60 nanowhiskers/WO3 nanocomposites were characterized by X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. UV-vis spectroscopy was used to evaluate the performance of the C60 nanowhiskers/WO3 nanocomposites as a photocatalyst in the degradation of organic dyes, such as methylene blue (MB) and brilliant green (BG) under ultraviolet light (254 nm).

Keywords: C60 nanowhiskers, WO3 nanoparticles, C60 nanowhiskers/WO3 nanocomposites, photocatalyst, degradation of organic dyes

Introduction

The pollution and destruction of the environment all around the world are issues of increasing concern in today’s society.1-4 There is a need for an effective method to remove pollutants.5-9 Photocatalysis has been widely used as a novel treatment for destroying organic pollutants. Some researchers have demonstrated the advantages of using modified carbon-based semiconductors as photocatalysts, including their strong absorption of visible light and high photocatalytic activity.10,11

A new type of C60 that takes the form of needle-like crystals, C60 nanowhiskers, was synthesized via liquid-liquid interfacial precipitation (LLIP), where the nanowhiskers nucleate at the interface between a toluene solution saturated with C60 and isopropyl alcohol.12-15 The needle crystal of C60 nanowhiskers has hexagonal rod shape and diameters ranging from 0.5 to 100 μm. The synthesized single crystal ferroelectric nanowires (FNWs) were less than 1 μm in diameter and greater than 100 μm in length.14,16,17

Metal oxide semiconductor photocatalysts have attracted much attention because of their potential applicability to the treatment of wastewater through the photocatalytic degradation of organic compounds. In previous studies, a range of metal oxide semiconductor materials, such as TiO2, CdS, ZnS, ZnO, and WO3, have been used to investigate the photocatalytic reduction of pollutants in water.18,19

WO3 nanoparticles are a versatile material that has attracted considerable interest because of its wide-ranging applications in various fields of technology, including electrochromic devices, photocatalysis, gas sensors, and lithium-ion batteries.20-23 WO3 nanoparticles have attracted considerable interest because of their photoactive properties, such as their wide response to the solar spectrum due to the size of their band gap (2.8 eV). WO3 nanoparticles are recognized as not only an important visible-light-responsive photocatalyst but also an excellent electron storage material.24-28

Experimental

1. Chemicals

The organic dyes, methylene blue (MB) and brilliant green (BG), and ammonium metatungstate hydrate were purchased.
from Sigma-Aldrich Co.. Ethanol and tetrahydrofuran (THF) were obtained from Samchun Chemicals Co.. C$_{60}$ was supplied by Tokyo Chemical Industry Co..

2. Instruments

An electric furnace (Ajeon Heating Industry Co.) was used to heat the samples, such as C$_{60}$ nanowhiskers, WO$_3$ nanoparticles, and C$_{60}$ nanowhiskers/WO$_3$ nanocomposites. A UV lamp (8 W, 254 nm, 77202 Marne La Valee-Cedex1 France) was used as the ultraviolet light source.

The solid state product was calcined in an electric furnace and the resulting solution was heated for 4 h on a hot plate.

The surface of the C$_{60}$ nanowhiskers/WO$_3$ nanocomposites was observed by scanning electron microscopy (SEM, JEOL Ltd., JSM-6510) at accelerating voltages of 0.5 to 15 kV. The morphology and particle size of the sample were examined with transmission electron microscopy (TEM, JEM-2010, JEOL Ltd.) at an acceleration voltage of 200 kV. The crystal structures of the C$_{60}$ nanowhiskers, WO$_3$ nanoparticles, and C$_{60}$ nanowhiskers/WO$_3$ nanocomposites were examined by X-ray diffraction (XRD, Bruker, D8 Advance) using Cu K$_\alpha$ radiation and a secondary monochromator (V = 40 kV, A = 40 mA, Ni filter). UV-vis spectroscopy (Shimadzu UV-1601PC) was performed to characterize the nanomaterials and assess their photocatalytic activity.

3. Synthesis of C$_{60}$ nanowhiskers/WO$_3$ nanocomposites

In a typical experiment, the C$_{60}$ nanowhiskers/WO$_3$ nanocomposites were prepared with a mass ratio of 1:1. The mixture was dissolved in 10 mL of THF with constant stirring for 30 min. The resulting solution was poured into a vessel, dried to vaporize the organic solvent for 1 h and heated at 800 K in an electric furnace under an argon gas atmosphere for 2 h to obtain the C$_{60}$ nanowhiskers/WO$_3$ nanocomposites.

4. Photocatalytic degradation of organic dyes with C$_{60}$ nanowhiskers/WO$_3$ nanocomposites

The photocatalytic activity of the C$_{60}$ nanowhiskers/WO$_3$ nanocomposites was examined using solutions of MB and BG. 5 mg of the C$_{60}$ nanowhiskers/WO$_3$ nanocomposites were dispersed into two 10 mL vials of water containing 0.01 mM of either MB or BG. Each vial was irradiated with ultraviolet light at 254 nm. The degradation of the MB and BG solutions with the C$_{60}$ nanowhiskers/WO$_3$ nanocomposites as a photocatalyst were observed by UV-vis spectroscopy.

Results and Discussion

Figure 1 shows SEM images of (a) the synthesized C$_{60}$ nanowhiskers, (b) the synthesized WO$_3$ nanoparticles and (c) the C$_{60}$ nanowhiskers/WO$_3$ nanocomposites. The C$_{60}$ nanowhiskers showed needle-like rod morphology. The WO$_3$ nanoparticles showed an irregular hexagonal structure and a rock nanobrick-like morphology. The WO$_3$ nanoparticles were located above the C$_{60}$ nanowhiskers, which had a needle-like rod morphology in the C$_{60}$ nanowhiskers/WO$_3$ nanocomposites.

Figure 2 shows TEM images of (a) the synthesized C$_{60}$ nanowhiskers, (b) the synthesized WO$_3$ nanoparticles and (c) the C$_{60}$ nanowhiskers/WO$_3$ nanocomposites. The C$_{60}$ nanowhiskers were grown by the LLIP method and had a needle-like rod morphology. The WO$_3$ nanoparticles showed an irregular, broken, rock-like morphology. The C$_{60}$ nanowhiskers/WO$_3$ nanocomposites showed an agglomerated state, where the WO$_3$ nanoparticles were adsorbed on the C$_{60}$ nanowhiskers.

Figure 3 shows the XRD patterns of (a) the synthesized C$_{60}$ nanowhiskers, (b) the synthesized WO$_3$ nanoparticles and (c) the C$_{60}$ nanowhiskers/WO$_3$ nanocomposites. The C$_{60}$ nanow-
Figure 1. SEM images of the synthesized (a) C$_{60}$ nanowhiskers, (b) WO$_3$ nanoparticles, and (c) C$_{60}$ nanowhiskers/WO$_3$ nanocomposites.

Figure 2. TEM images of the synthesized (a) C$_{60}$ nanowhiskers, (b) WO$_3$ nanoparticles, and (c) C$_{60}$ nanowhiskers/WO$_3$ nanocomposites.

The whiskers have peaks at 2θ angles of 10.82°, 17.69°, 20.78°, 28.09°, 30.49°, and 32.80°, which were assigned to the (111), (220), (311), (420), (422), and (333) planes. The XRD patterns...
tern of the WO$_3$ nanoparticles has peaks at 2θ angles of 23.16°, 23.36°, 24.45°, 33.52°, 34.17°, 35.62°, 41.77°, 45.65°, 47.30°, 50.57°, 55.83°, 61.42°, 67.31°, 76.47°, 82.24°, and 86.08°, which were assigned to the (001), (020), (200), (101), (021), (220), (121), (221), (311), (002), (321), (401), (421), (322), (422), and (303) planes. The XRD pattern of the C$_{60}$ nanowhiskers/WO$_3$ nanocomposites has peaks at 2θ angles of 23.16°, 23.79°, 24.32°, 26.74°, 33.48°, 34.15°, 35.66°, 41.69°, 45.71°, 47.30°, 50.57°, 55.79°, 61.40°, 67.02°, 76.53°, 82.50°, and 86.14° due to the WO$_3$ nanoparticles, which were assigned to the (001), (020), (200), (101), (021), (220), (121), (221), (311), (002), (321), (401), (421), (322), (422), and (303) planes. The XRD pattern of the C$_{60}$ nanowhiskers/WO$_3$ nanocomposites has peaks at 2θ angles of 23.16°, 23.79°, 24.32°, 26.74°, 33.48°, 34.15°, 35.66°, 41.69°, 45.71°, 47.30°, 50.57°, 55.79°, 61.40°, 67.02°, 76.53°, 82.50°, and 86.14° due to the WO$_3$ nanoparticles, which were assigned to the (001), (020), (200), (101), (021), (220), (121), (221), (311), (002), (321), (401), (421), (322), (422), and (303) planes. The XRD pattern of the C$_{60}$ nanowhiskers/WO$_3$ nanocomposites has peaks at 2θ angles of 23.16°, 23.79°, 24.32°, 26.74°, 33.48°, 34.15°, 35.66°, 41.69°, 45.71°, 47.30°, 50.57°, 55.79°, 61.40°, 67.02°, 76.53°, 82.50°, and 86.14° due to the WO$_3$ nanoparticles, which were assigned to the (001), (020), (200), (101), (021), (220), (121), (221), (311), (002), (321), (401), (421), (322), (422), and (303) planes. The XRD pattern of the C$_{60}$ nanowhiskers/WO$_3$ nanocomposites has peaks at 2θ angles of 23.16°, 23.79°, 24.32°, 26.74°, 33.48°, 34.15°, 35.66°, 41.69°, 45.71°, 47.30°, 50.57°, 55.79°, 61.40°, 67.02°, 76.53°, 82.50°, and 86.14° due to the WO$_3$ nanoparticles, which were assigned to the (001), (020), (200), (101), (021), (220), (121), (221), (311), (002), (321), (401), (421), (322), (422), and (303) planes. The XRD pattern of the C$_{60}$ nanowhiskers/WO$_3$ nanocomposites has peaks at 2θ angles of 23.16°, 23.79°, 24.32°, 26.74°, 33.48°, 34.15°, 35.66°, 41.69°, 45.71°, 47.30°, 50.57°, 55.79°, 61.40°, 67.02°, 76.53°, 82.50°, and 86.14° due to the WO$_3$ nanoparticles, which were assigned to the (001), (020), (200), (101), (021), (220), (121), (221), (311), (002), (321), (401), (421), (322), (422), and (303) planes. The XRD pattern of the C$_{60}$ nanowhiskers/WO$_3$ nanocomposites has peaks at 2θ angles of 23.16°, 23.79°, 24.32°, 26.74°, 33.48°, 34.15°, 35.66°, 41.69°, 45.71°, 47.30°, 50.57°, 55.79°, 61.40°, 67.02°, 76.53°, 82.50°, and 86.14° due to the WO$_3$ nanoparticles, which were assigned to the (001), (020), (200), (101), (021), (220), (121), (221), (311), (002), (321), (401), (421), (322), (422), and (303) planes.
(422), (342), and (303) planes, and peaks at 10.87°, 17.70°, 20.81°, 28.04°, 30.80°, and 32.81° due to the C_{60} nanowhiskers, which were assigned to the (111), (220), (311), (420), (422), and (333) planes.

Figure 4 shows the UV-vis spectra of (a) the C_{60} nanowhiskers which were synthesized using the LLIP method, the degraded (b) methylene blue (MB) and (c) brilliant green (BG) solution with the C_{60} nanowhiskers/WO_{3} nanocomposites under ultraviolet irradiation at 254 nm. The UV-vis spectra of the C_{60} nanowhiskers which were dissolved in toluene revealed peaks at $\lambda_{\text{max}} = 542$ nm, 597 nm and 622 nm. As a result, MB solution was more effectively degraded than BG solution, comparing the intensity of absorbance of each sample when using the C_{60} nanowhiskers/WO_{3} nanocomposites as a photocatalyst.

Conclusion

The C_{60} nanowhiskers had a needle-like rod morphology with a length of 6 μm. The WO_{3} nanoparticles had an irregular, broken, rock-like morphology and were less than 2 nm in size. In the C_{60} nanowhiskers/WO_{3} nanocomposites, the WO_{3} nanoparticles were attached to the sides of the C_{60} nanowhiskers. The length of C_{60} nanowhiskers decreased during calcination, because they might have been broken to a smaller size. The photocatalytic degradation with the C_{60} nanowhiskers/WO_{3} nanocomposites was more efficient for MB than BG.

Acknowledgments

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References

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