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Synthesis of SnO_2-Mn-C_{60} Nanocomposites and Their Photocatalytic Activity for Degradation of Organic Dyes

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Abstract: Nanocomposites based on SnO_2-Mn were synthesized by the reaction of tin (II) chloride dihydrate and manganese (II) chloride tetrahydrate at a molar ratio of 10:1 in the presence of ammonium hydroxide at 80°C. The SnO_2-Mn nanocomposites were stirred with fullerene [C_{60}] in a mass ratio of 2:1 in tetrahydrofuran to prepare SnO_2-Mn-C_{60} nanocomposites; these nanocomposites were obtained upon heating the mixture of SnO_2-Mn nanocomposites and fullerene [C_{60}] in an electric furnace at 700°C for 2 h. The synthesized SnO_2-Mn-C_{60} nanocomposites were confirmed through various characterization methods such as X-ray diffraction and scanning electron microscopy. The photocatalytic activities of the SnO_2-Mn-C_{60} nanocomposites were demonstrated by the degradation of the organic dyes BG, MB, MO, and RhB under 254 nm irradiation and evaluated using UV-Vis spectrophotometry.

Keywords: SnO_2-Mn-C_{60} nanocomposites, photocatalytic activities, degradation of the organic dyes, UV-Vis spectrophotometry

Introduction

The synthesis and characterization of semiconductor materials are gaining popularity important functional materials such as dielectrics, polymers, magnetics, and semiconductors due to their good optical properties.[1-3] In recent years, the investigation of nanocrystalline semiconductors focused on enhancing the optical properties of nanocrystalline semiconductors have been conducted.[4]

Tin oxide (SnO_2), an n-type semiconductor, is one of the most interesting and well-known oxide semiconductor materials. Tin oxide has a rutile crystalline structure, and exhibits numerous engaging chemical and physical properties. The band-gap energy of tin oxide is 3.6 eV.[4-7] Nanostructured tin oxide is a technologically versatile and important semiconductor. Especially, the optical properties of tin oxide have been studied with great interests for industrial application. Due to its higher optical transparency, remarkable chemical stability, and electrical conductivity, tin oxide has been utilized for various applications such as optoelectronic devices, liquid crystal display transistors, solar cells, oxidation catalysis, gas sensors, transparent conducting electrodes, and spintronics.[8-12]

Nanoscale tin oxide/has been synthesized by several methods such as sol-gel, gel-combustion, hydrothermal, chemical precipitation, and solvothermal technology, etc.[13-15] Among the various technology, the sol-gel method has been known as one of the most effective methods since it allows the structural and surface properties of nanomaterials to be controlled.[16] The chemical precipitation method is a simple and promising because the particle size and morphological properties of the nanoparticles can be controlled by the reaction conditions such as concentration, pH, reaction temperature.[13]

Recently, great number of studies have been carried out tin oxide doping with a proper activator for the modification of the optical, magnetic, and electrochemical properties of metal oxide semiconducting materials.[5] It has been proved that transition metal ion doping is an effective method to regulate the transport performance of carriers, surface properties, and energy levels of semiconductors.[17] Due to the fact that doping with Mn results in an electronic band structure variation of SnO_2 and shows a large magnetoresistance, most of the previous studies have been focused on the preparation of Mn-doped SnO_2.[18,19] So far, most researchers have focused on the magnetic properties of Mn-doped SnO_2, but the optical and

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catalytic properties of Mn-doped SnO_2 nanoparticles not being investigated widely.[5,8] Detailed studies about these properties are needed to explore the potential applications of this nanomaterial.

The organic pollutants generated by chemicals from synthetic dyes and pigments are the most refractory pollutants in industrial wastewater, and cause many environmental problems. In order to remove these pollutants, various methods have been considered and much effort has been devoted.[20,21] Traditional methods such as active sludge, adsorption on activated carbon, combined coagulation, and electrochemical oxidation have proved to be adequate.[22] Nowadays, the use of photocatalytic degradation is a promising method to remove these organic pollutants and has attracted the interest of many researchers.[23,24] Photocatalytic degradation is induced by electron-hole pairs, which are generated in semiconducting materials under illumination by light.[23-25] Furthermore, it should be noted that the photocatalytic activity of semiconducting materials can be enhanced by combining semiconducting materials with nanocarbon materials. Due to the electron-accepting performance of fullerene [C_{60}], many C_{60}-modified semiconducting materials have been prepared for the photocatalytic degradation of organic dyes.[26,27]

Therefore, in the present study, we report the doping of SnO_2 nanoparticles with Mn ions using a simple method. The synthesis of SnO_2-Mn-C_{60} nanocomposites was achieved by calcining a mixture of SnO_2-Mn nanocomposites and fullerene [C_{60}] in an electric furnace. The structural and morphological properties were studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The photocatalytic activities of the SnO_2-Mn-C_{60} nanocomposites were characterized by the degradation of the organic dyes BG, MB, MO, and RhB, using UV-Vis spectrophotometry.

Experimental

1. Materials

Tin (II) chloride dihydrate [$SnCl_2{\cdot}2H_2O$] was obtained from Duksan Pharmaceutical Co., Ltd. Manganese (II) chloride tetrahydrate [$MnCl_2{\cdot}4H_2O$], ammonium hydroxide [$NH_3{\cdot}H_2O$], brilliant green (BG), and methyl orange (MO) were supplied by Sigma-Aldrich. Fullerene [C_{60}] was purchased from Tokyo Chemical Industry Co., Ltd. Methylene blue $3H_2O$ (MB), Rhodamine B (RhB), and tetrahydrofuran (THF) were obtained from Samchun Chemicals. All chemical materials were used as received without any further purification or treatment.

2. Synthesis of SnO_2-Mn-C_{60} nanocomposites

In a typical procedure SnO_2-Mn nanocomposites were synthesized by adding $MnCl_2{\cdot}4H_2O$ to 100 ml of 0.01 mol dm^{-3} $SnCl_2{\cdot}2H_2O$ aqueous solution in a molar ratio of 1:10 ($MnCl_2{\cdot}4H_2O$/$SnCl_2{\cdot}2H_2O$). The mixture was then stirred for 10 min at 80°C, following which 3 ml of $NH_3{\cdot}H_2O$ was added dropwise to obtain a white precipitate. After addition, the resulting solution was continuously stirred at 80°C for 30 min. The resulting precipitate was centrifuged and washed 5 times with distilled water and then dried at 80°C for 12 h in an electric oven to collect the SnO_2-Mn nanocomposites. Subsequently, the resulting SnO_2-Mn nanocomposites were mixed with fullerene [C_{60}] at a 2:1 mass ratio in THF (10 mL) and then calcined in an electric furnace (Ajeon Heating Industry Co., Ltd.) at 700°C for 2 h under an inert atmosphere of argon gas to form SnO_2-Mn-C_{60} nanocomposites.

3. Characterization of samples

The structures of the SnO_2-Mn nanocomposites and SnO_2-Mn-C_{60} nanocomposites were characterized by XRD with Cu Kα radiation (Bruker, D8 Advance, λ=1.54178 Å). SEM (JEOL Ltd, JSM-6510) at an accelerating voltage of 0.5 to 30 kV was used to examine the morphological characterization of the samples and particle shapes. UV-Vis spectra of photocatalytic degradations were recorded using a UV-Vis spectrophotometer (Shimadzu UV-1619PC).

4. Evaluation of the photocatalytic activity

The photocatalytic activity of the prepared SnO_2-Mn-C_{60} nanocomposites was demonstrated by monitoring the degradation of the various organic dyes including BG (1.32×10^{-2} mmol/L), MB (1.05×10^{-2} mmol/L), MO (6.11×10^{-2} mmol/L), and RhB (1.00×10^{-2} mmol/L). In a typical experiment, a 10 ml glass vial was charged with a 10 ml organic dye solution of each of the foregoing dyes, each having an absorbance value of 1.0. As a photocatalyst, 5 mg SnO_2-Mn-C_{60} nanocomposites were added into the organic dye solution. To achieve an adsorption-desorption equilibrium between the organic dye and photocatalyst, the glass vial was kept in a

dark environment for 30 min. Then, the reactor was irradiated by a UV-lamp (8 W, 254 nm, 77202 Marne-la-Vallée-cedex 1, France). The process of photocatalytic degradation was analyzed using UV-Vis spectrophotometry by monitoring at 20 min interval.

Results and Discussion

1. XRD and SEM analysis

The XRD patterns of the SnO_2-Mn nanocomposites and SnO_2-Mn-C_{60} nanocomposites are shown in Figure 1a and

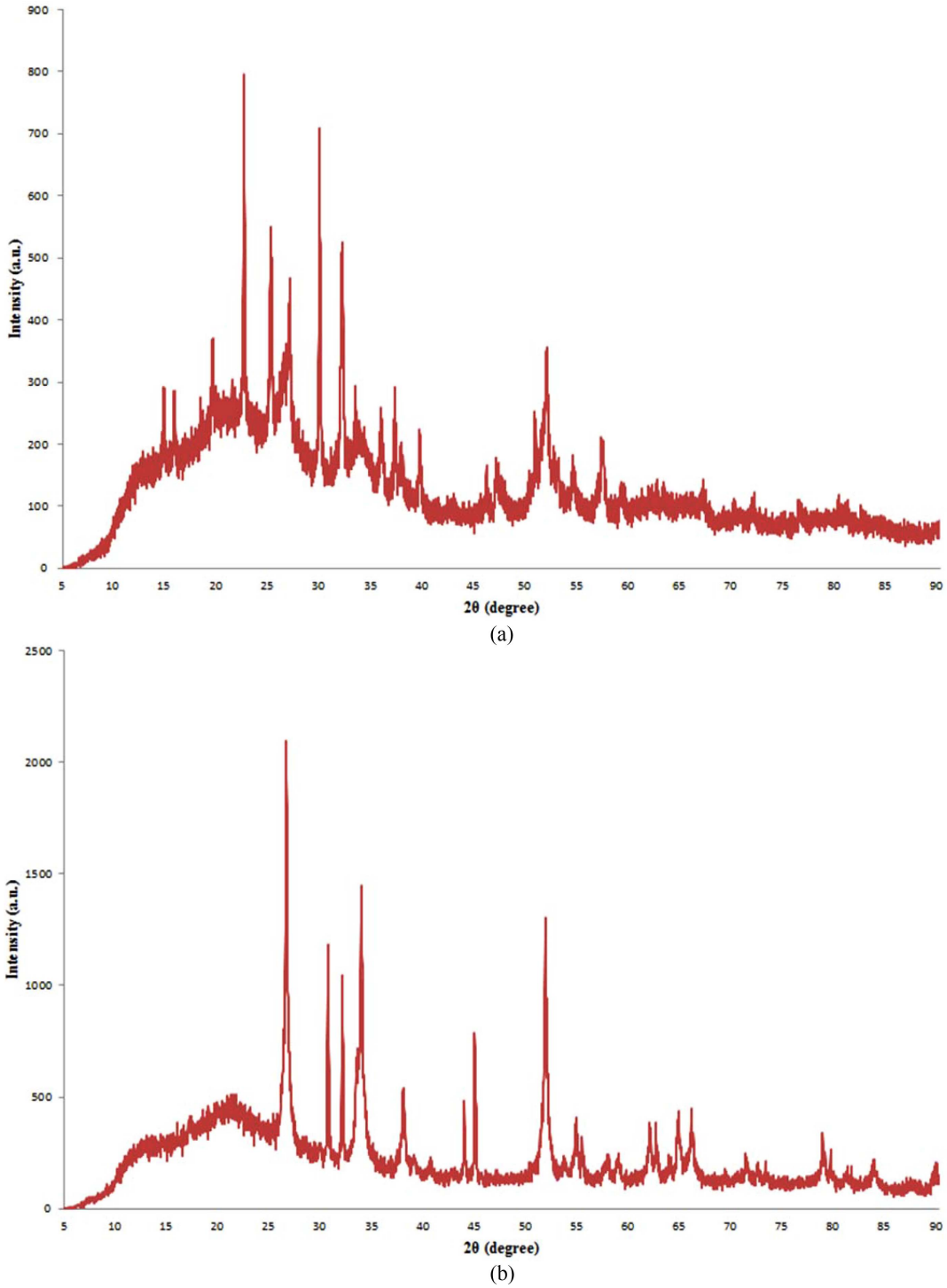


Figure 1. (a) XRD pattern of SnO_2-Mn nanocomposites. (b) XRD pattern of SnO_2-Mn-C_{60} nanocomposites.

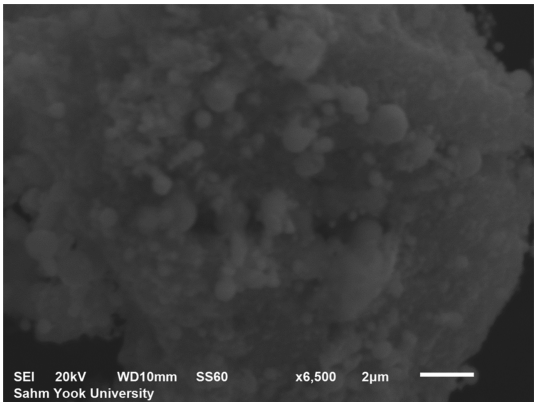


Figure 2. SEM image of SnO_2-Mn-C_{60} nanocomposites.

1b, respectively. The characteristic peaks at 2θ = 26.6°, 33.9°, 38.0°, 51.8°, 54.8°, 57.9°, 66.0°, 71.3°, and 78.7° correspond to the (110), (101), (200), (211), (220), (002), (301), (202), and (321) crystal planes of SnO_2-Mn, respectively.[4,28] The XRD patterns of C_{60} showed a small peak at 2θ = 21.8° correspond to the (311) crystal plane of C_{60} powders, respectively (JCPDS file No.44-0558).[29] The XRD patterns also show that the SnO_2-Mn nanocomposites and SnO_2-Mn-C_{60} nanocomposites have good crystallinity and large surface areas.

Figure 2 shows the SEM image of the SnO_2-Mn-C_{60} nano-

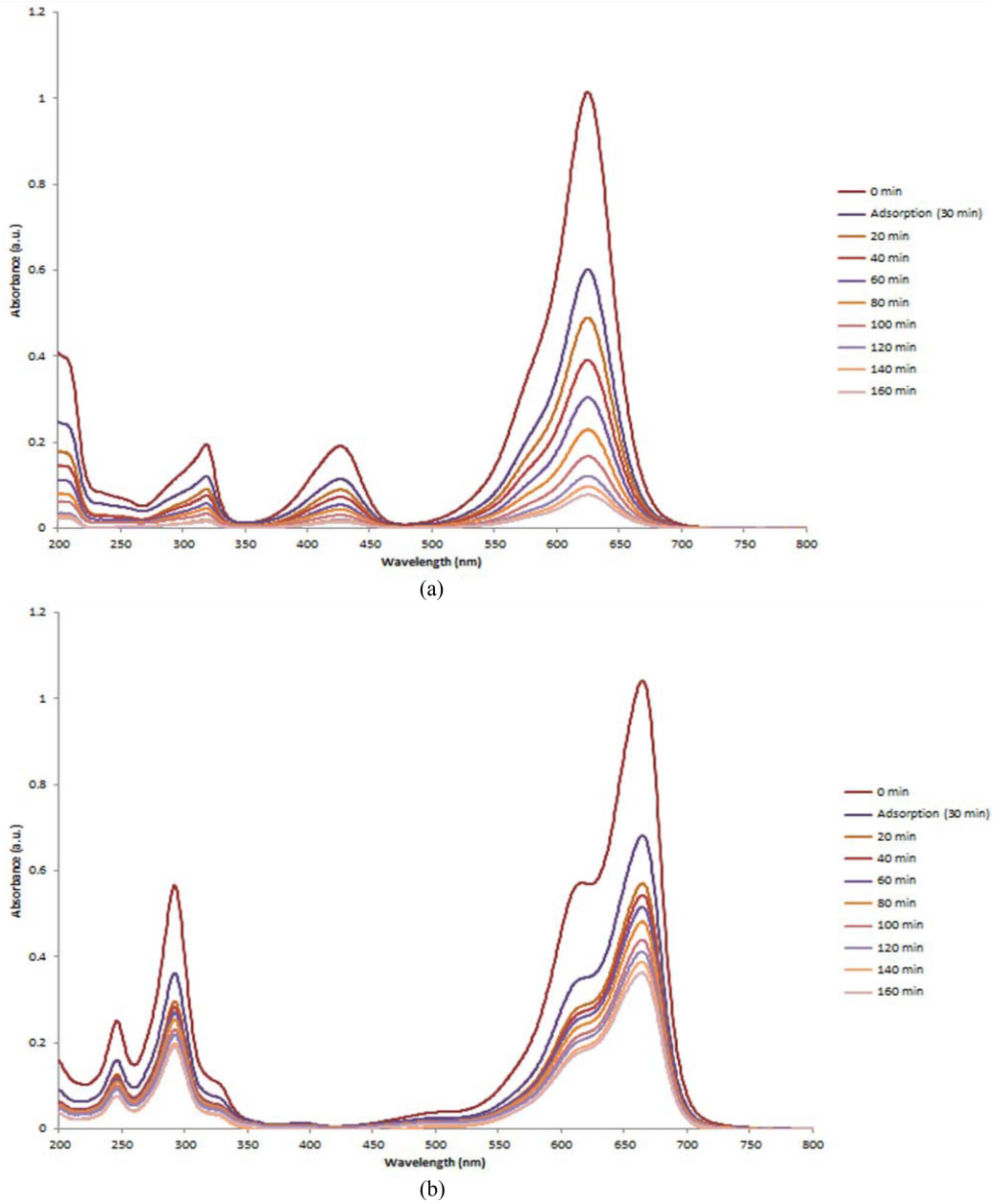
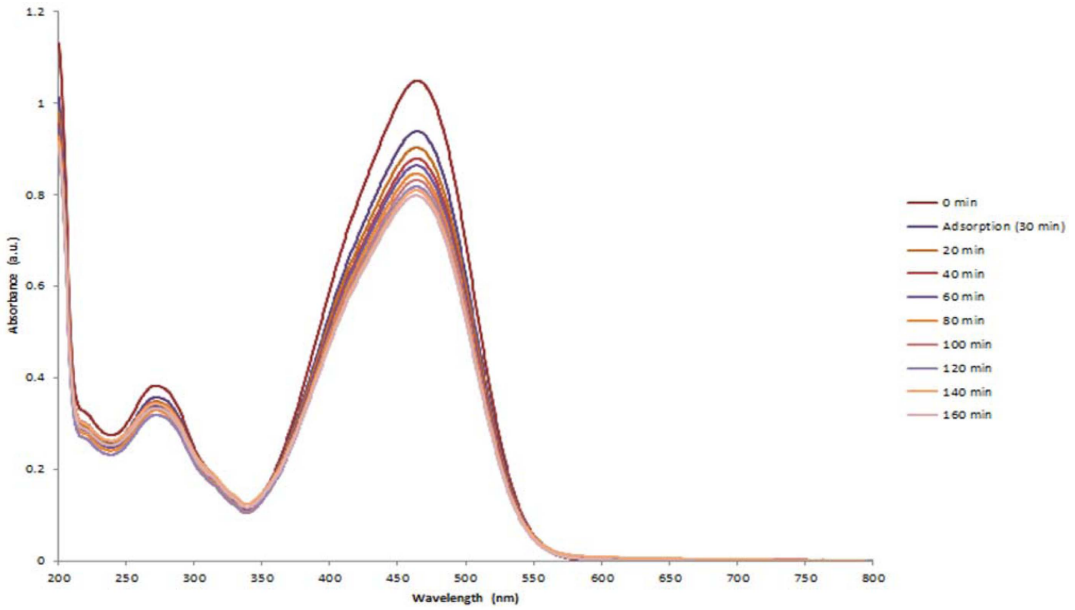


Figure 3. (a) UV-vis spectrum of the BG solution with SnO_2-Mn-C_{60} nanocomposites as photocatalyst under UV lamp illumination at 254 nm. (b) UV-vis spectrum of the MB solution with SnO_2-Mn-C_{60} nanocomposites as photocatalyst under UV lamp illumination at 254 nm.

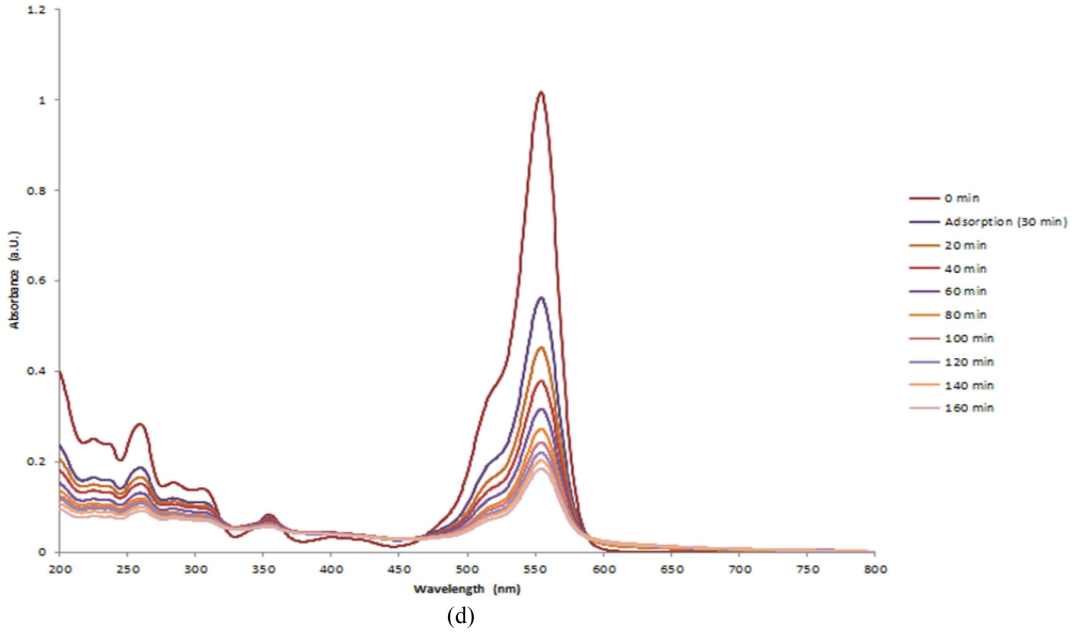
composites. The spherical morphology of the SnO_2-Mn nanocomposites is clearly visible in Figure 2, and it can also be seen that the SnO_2-Mn nanocomposites adhere to the surface of fullerene [C_{60}] with a spheroidal morphology. It should be noted that the particle size of SnO_2-Mn nanocomposites is comparatively smaller than that of fullerene [C_{60}].

2. Photocatalytic performance

In order to investigate the photocatalytic activities of the synthesized samples, the degradation of the organic dyes BG, MB, MO, and RhB was performed by using SnO_2-Mn-C_{60} nanocomposites as photocatalyst under UV lamp illumination at 254 nm. Figure 3a shows the degradation of BG using SnO_2-Mn-C_{60} nanocomposites as photocatalyst. Figure 3b displays the UV-Vis spectra of the degrading MB solution. Figure 3c shows the UV-Vis spectra of the degradation of MO. Finally, Figure 3d is the UV-Vis spectra of the degradation of RhB. This investigation indicated that the absorbance values of the organic dyes decreased according to



(c)



(d)

Figure 3. (c) UV-vis spectrum of the MO solution with SnO_2-Mn-C_{60} nanocomposites as photocatalyst under UV lamp illumination at 254 nm. (d) UV-vis spectrum of the RhB solution with SnO_2-Mn-C_{60} nanocomposites as photocatalyst under UV lamp illumination at 254 nm.

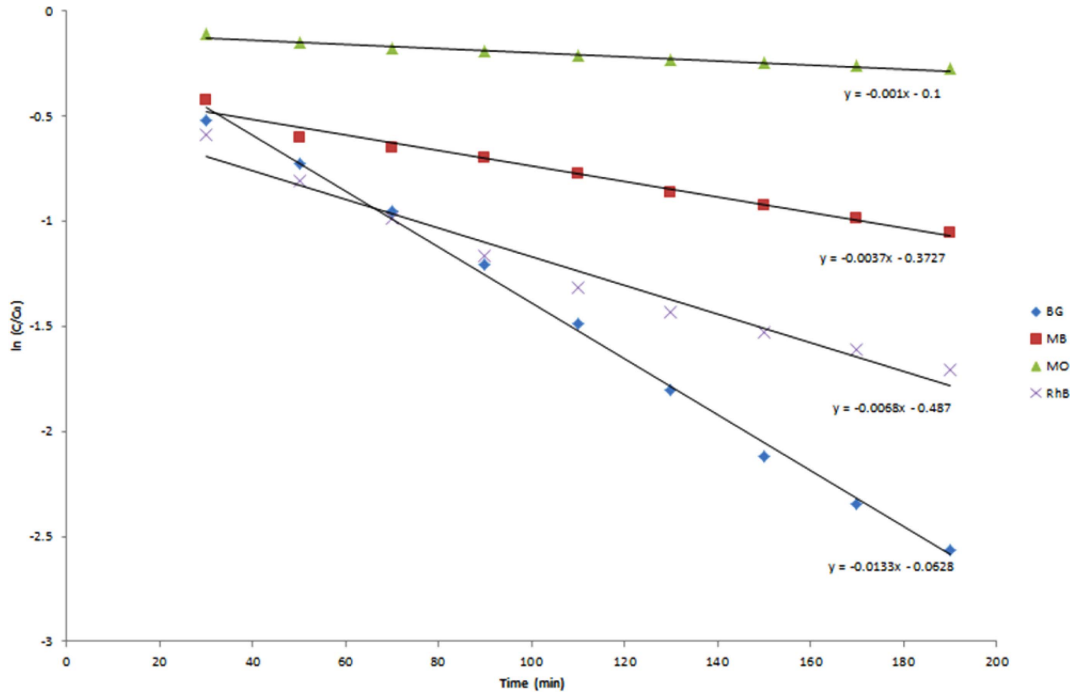


Figure 4. Kinetics study of the photocatalytic degradation of organic dyes with SnO_2-Mn-C_{60} nanocomposites as photocatalyst under 254 nm UV irradiation.

increasing irradiation time. As a result, the solution color of the organic dyes changed from dark to light color.

3. Kinetic study

Results of the above investigations show that the value of the concentration ratio ln(C/C_0) is proportional to the irradiation time. In order to determine the degradation rate of the organic dyes when using SnO_2-Mn-C_{60} nanocomposites as photocatalyst under UV lamp illumination at 254 nm, the Langmuir-Hinshelwood model was used as a model fit for the pseudo-first-order reaction. This model has been applied to the photocatalytic degradation kinetics of many organic compounds in many papers, and so it was suitable to be used for the kinetics study of photocatalytic degradation.[30,31] The equation can be written as follows:

$$\ln(C/C_0) = -Kap \cdot t$$

where C/C_0 is the concentration ratio of the organic dye solution at a measuring time t to the initial concentration. The reaction rate constant was *Kap*. Figure 4 shows that the order of photocatalytic degradation of the organic dyes with SnO_2-Mn-C_{60} nanocomposites was BG > RhB > MB > MO. It can be said that the degradation rate of BG was the fastest and the degradation rate of MO was the slowest when using SnO_2-Mn-C_{60} nanocomposites as photocatalyst under ultraviolet irradiation at 254 nm.

Conclusion

In summary, Mn ion-doped SnO_2 nanoparticles were successfully synthesized using a chemical precipitation method, and SnO_2-Mn-C_{60} nanocomposites were prepared by heating SnO_2-Mn nanocomposites and fullerene [C_{60}] at 700°C for 2 h. The structural and crystalline analysis were carried out by XRD. SEM analysis revealed that SnO_2-Mn nanocomposites were adhered to the surface of fullerene [C_{60}] with a large spheroidal morphology. The photocatalytic activity of the synthesized SnO_2-Mn-C_{60} nanocomposites was examined by the degradation of organic dyes BG, MB, MO, and RhB under UV lamp illumination at 254 nm. The UV-Vis spectra showed that the order of photocatalytic degradation of the organic dyes with SnO_2-Mn-C_{60} nanocomposites was BG > RhB > MB > MO.

Acknowledgements

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References

1. A. Sharma, M. Varshney, S. Kumar, K. D. Verma, and R. Kumar, "Magnetic properties of Fe and Ni doped SnO_2 nanoparticles", *Nanomater. Nanotechno.*, **1**, 24 (2011).
2. G. A. Prinz, "Magnetoelectronics", *Science*, **282**, 1660 (1998).
3. S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. V. Molnar, M. L. Roukes, A. Y. Chtcheljanova, and D. M. Treger, "Spintronics: A Spin-Based Electronics Vision for the Future", *Scinece*, **294**, 1488 (2001).
4. A. Azam, A. S. Ahmed, S. S. Habib, and A. H. Naqvi, "Effect of Mn doping on the structural and optical properties of SnO_2 nanoparticles", *J. Alloy. Compd.*, **523**, 83 (2012).
5. N. Salah, S. Habib, A. Azam, M. S. Ansari, and W. M. AL-Shawafi, "Formation of Mn-doped SnO_2 nanoparticles via the microwave technique: structural, optical and electrical properties", *Nanomater. Nanotechno.*, DOI: 10.5772/62520 (2016).
6. B. Liu, C. W. Cheng, R. Chen, Z. X. Shen, H. J. Fan, and H. D. Sun, "Fine structure of ultraviolet photoluminescence of tin oxide nanowires", *J. Phys. Chem. C*, **114**, 3407 (2010).
7. S. Mehraj, M. S. Ansari, and Alimuddin, "Structural, electrical and magnetic properties of (Fe, Co) co-doped SnO_2 diluted magnetic semiconductor nanostructures", *Physica E*, **65**, 84 (2015).
8. X. G. Chen, W. W. Li, J. D. Wu, J. Sun, K. Jiang, Z. G. Hu, and J. H. Chu, "Temperature dependence of electronic band transition in Mn-doped SnO_2 nanocrystalline films determined by ultraviolet-near-infrared transmittance spectra", *Mater. Res. Bull.*, **47**, 111 (2012).
9. R. S. Niranjan, Y. K. Hwang, D. K. Kim, S. H. Jhung, J. S. Chang, and I. S. Mulla, "Nanostructured tin oxide: Synthesis and gas-sensing properties", *Mater. Chem. Phys.*, **92**, 384 (2005).
10. S. C. Lee, J. H. Lee, T. S. Oh, and Y. H. Kim, "Fabrication of tin oxide film by sol-gel method for photovoltaic solar cell system", *Sol. Energ. Mat. Sol. C.*, **75**, 481 (2003).
11. W. L. Yu, W. W. Li, J. D. Wu, J. Sun, J. J. Zhu, M. Zhu, Z. G. Hu, and J. H. Chu, "Far-infrared-ultraviolet dielectric function, lattice vibration, and photoluminescence properties of diluted magnetic semiconductor $Sn_{1-x}Mn_xO_2$/c-sapphire nanocrystalline films", *J. Phys. Chem. C*, **114**, 8593 (2010).
12. A. Bouaine, N. Brihi, G. Schmerber, C. U. Bouillet, S. Colis, and A. Dinia, "Structural, optical, and magnetic properties of Co-doped SnO_2 powders synthesized by the co-precipitation technique", *J. Phys. Chem. C*, **111**, 2924 (2007).
13. B. Sathyaseelana, K. Senthilnathanb, T. Alagesanc, R. Jayaveld, and K. Sivakumara, "A study on structural and optical properties of Mn- and Co-doped SnO_2 nanocrystallites", *Mater. Chem. Phys.*, **124**, 1046 (2010).
14. H. Zhu, D. Yang, G. Yu, H. Zhang, and K. Yao, "A simple hydrothermal route for synthesizing SnO_2 quantum dots", *Nanotechnology*, **17**, 2386 (2006).
15. Y. Liu, F. Yang, and X. Yang, "Size-controlled synthesis and characterization of quantum-size SnO_2 nanocrystallites by a solvothermal route", *Colloid. Surface. A*, **312**, 219 (2008).
16. A. C. Bose, P. Thangadurai, and S. Ramasamy, "Grain size dependent electrical studies on nanocrystalline SnO_2", *Mater. Chem. Phys.*, **95**, 72 (2006).
17. N. Lavanya, E. Fazio, F. Neri, A. Bonavita, S. G. Leonardi, G. Neri, and C. Sekar, "Electrochemical sensor for simultaneous determination of ascorbic acid, uric acid and folic acid based on Mn-SnO_2 nanoparticles modified glassy carbon electrode", *J. Electroanal. Chem.*, **770**, 23 (2016).
18. G. Chen, W. W. Li, J. D. Wu, J. Sun, K. Jiang, Z. G. Hu, and J. H. Chu, "Temperature dependence of electronic band transition in Mn-doped SnO_2 nanocrystalline films determined by ultraviolet-near-infrared transmittance spectra", *Mater. Res. Bull.*, **47**, 111 (2012).
19. W. W. Li, J. J. Zhu, J. D. Wu, J. Sun, M. Zhu, Z. G. Hu, and J. H. Chu, "Composition and temperature dependence of electronic and optical properties in manganese doped tin dioxide Films on quartz substrates prepared by pulsed laser deposition", *ACS Appl. Mater. Interfaces*, **2**, 2325 (2010).
20. X. Chen and S. S. Mao, "Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications", *Chem. Rev.*, **107**, 2891 (2007).
21. Z. He, W. Que, J. Chen, X. Yin, Y. He, and J. Ren, "Photocatalytic degradation of methyl orange over nitrogen-fluorine codoped TiO_2 nanobelts prepared by solvothermal synthesis", *ACS Appl. Mater. Interfaces*, **4**, 6816 (2012).
22. A. M. K. El-ghonemy, "Waste energy recovery in sea water reverse osmosis desalination plants, Part-1: review", *Renew. Sust. Energ. Rev.*, **18**, 6 (2013).
23. K. Anandan and V. Rajendran, "Influence of dopant concentrations (Mn = 1, 2 and 3 mol %) on the structural, magnetic and optical properties and photocatalytic activities of SnO_2 nanoparticles synthesized via the simple precipitation process", *Superlattice. Microst.*, **85**, 185 (2015).
24. V. K. Sharma, T. M. Triantis, M. G. Antoniou, X. He, M. Pelaez, C. Han, W. Song, K. E. O'Shea, A. A. de la Cruz, T. Kaloudis, A. Hiskia, and D. D. Dionysiou, "Destruction of microcystins by conventional and advanced oxidation processes", *Sep. Purif. Technol.*, **91**, 3 (2012).
25. K. Hara, T. Horiguchi, T. Khinoshita, K. Sayama, H. Sugihara, and H. Arakawa, "Highly efficient photon-to-electron conversion with mercurochromesensitized nanoporous oxide semiconductor solar cells", *Sol. Energ. Mat. Sol. C.*, **64**, 115 (2000).

26. J. L. Li, J. W. Ko, and W. B. Ko, "Preparation and characterization of CeO_2-C_{60} nanocomposites and their application to photocatalytic degradation of organic dyes", *Asian J. Chem.*, **28**, 2020 (2016).
27. J. L. Li, J. W. Ko, and W. B. Ko, "Photocatalytic activities of carbon nanocapsules encircled by nickel nanoparticle composites to organic dyes degradation", *J. Ceram. Process. Res.*, **16**, 457 (2015).
28. S. Mehraj, M. S. Ansari, and Alimuddin, "Rutile-type Co doped SnO_2 diluted magnetic semiconductor nanoparticles: structural, dielectric and ferromagnetic behavior", *Physica B*, **430**, 106 (2013).
29. M. Ishikawa, S. Kamiya, S. Yoshimoto, M. Suzuki, D. Kuwahara, N. Sasaki, and K. Miura, "Nanocomposite materials of alternately stacked C_{60} monolayer and graphene", *J. Nanomater.*, **2010**, 891514 (2010).
30. N. S. Arul, D. Mangalaraj, and T. W. Kim, "Photocatalytic degradation mechanisms of CeO_2/Tb_2O_3 nanotubes", *Appl. Surf. Sci.*, **349**, 459 (2015).
31. S. K. Kansal, G. Kaur, and S. Singh, "Studies on the photocatalytic degradation of 2,3-dichlorophenol using different oxidants in aqueous solutions", *React. Kinet. Catal. L.*, **98**, 177 (2009).