Elastomers and Composites
Vol. 52, No. 2, pp. 131~135 (June 2017)

Print ISSN 2092-9676/Online ISSN 2288-7725
DOI: https://doi.org/10.7473/EC.2017.52.2.131

Photocatalytic Degradation of 3-Nitrophenol with ZnO Nanoparticles under UV Irradiation

Jiulong Li and Weon Bae Ko†

Department of Chemistry, Sahmyook University, Seoul 139-742, Korea

(Received May 22, 2017, Revised May 29, 2017, Accepted June 1, 2017)

Abstract: Zinc nitrate hexahydrate [$Zn(NO_3)\cdot 6H_2O$] and sodium hydroxide [NaOH] were used as source reagents in the preparation of ZnO nanoparticles in an aqueous solution containing deionized water and ethanol in a ratio of 2:5 (*v/v*). ZnO nanoparticles were heated in an electric furnace at 700°C for 2 h under an atmosphere of inert argon gas. The morphological and structural properties of the nanoparticles were characterized by scanning electron microscopy (SEM) and powder X-ray diffractometry (XRD). UV-vis spectrophotometry was used to analyze the photocatalytic degradation of 3-nitrophenol with ZnO nanoparticles as photocatalyst under ultraviolet irradiation at 254 nm. Evaluation of the kinetic of the photocatalytic degradation of 3-nitrophenol indicated that the degradation of 3-nitrophenol with ZnO nanoparticles obeyed the pseudo-first order reaction rate model.

Keywords: ZnO nanoparticles, photocatalytic degradation, 3-nitrophenol, ultraviolet irradiation, kinetic

Introduction

Nitroaromatic compounds are amongst the most refractory pollutants in industrial wastewater.[1] Among these nitroaromatic compounds, the isomers of nitrophenol have broad applications for herbicides, dyes, plasticizers and pesticides.[2-4] Nitrophenols can contaminate drinking water sources, taint fish meat, and cause damage to the ecosystem and human health.[1] All three isomers, o-nitrophenol (o-NP), m-nitrophenol (m-NP) and p-nitrophenol (p-NP) are toxic, teratogenic, mutagenic and cancerogenic.[5]

Therefore, the removal of these organic pollutants has become a pressing issue that must be solved. Various methods such as biological degradation, physical treatment, electrochemical oxidation, and photocatalytic oxidation have been proposed to remove nitrophenols from the environment.[6-9] However, due to the toxicity of nitrophenols towards microorganisms, biodegradation is inefficient.[10] Physical treatment can be performed by utilizing physical adsorption to reduce the content of pollutants in wastewater.[11] It was well known that the process of adsorption is nondestructive, so to completely remove the organic pollutants, a further step is needed. Therefore, a combined chemical-physical process is the conventional treatment in industrial wastewater for organic pollutants.[12,13]

In recent decades, with the development of nanotechnology, increasing numbers of nanomaterials have been synthesized for applications in optics, sensors, catalysts, photocatalysts and information storage.[14] Many metal nanoparticles or metal oxide nanoparticles have been synthesized as catalysts for the reduction of organic compounds with suitable reducing agents like $NaBH_4$.[15,16] Murettin Sahiner et al. investigated the reduction of nitrophenols using cobalt nanoparticles.[14] Similarly, the degradation of nitrophenols by irradiated light on TiO_2 was reviewed by Maurino et al..[9] In the research of Binxia Zhao et al., 4-nitrophenol was degraded by Fe-TiO_2 as a heterogeneous photo-Fenton catalyst.[2]

Recently, researchers have applied photocatalytic processes to wastewater treatment.[17,18] Photocatalytic degradation, as a chemical-physical process, represents a promising technique for the degradation of organic pollutants because the catalysts used in this process are mostly nontoxic.[12,19] The photodegradation of nitrophenols under UV irradiation mainly involves the reaction of nitrophenols with oxygen in aqueous solution to form carbon oxide and water.[20] Investigations of the photocatalytic degradation of nitrophenols by using semiconducting nanomaterials has attracted much attention due to their many other potential applications toward air and water

†Corresponding author E-mail: kowbsahmyook@syu.ac.kr

purification. For example, Chen et al. reported that 4-nitrophenol can be photodegraded in a TiO_2 suspension which has also been extensively used as a semiconductor catalyst.[20] ZnO also has potential applications in similar fields due to its similar band gap energy when compared with TiO_2.[21] The band gap energy of TiO_2 is 3.2 eV, and the band gap energy of ZnO ranges between 3.2 and 3.3 eV.[22] Metal oxide semiconductors are becoming increasingly popular photocatalysts and ZnO has been frequently used due to its low cost, non-toxicity and excellent photocatalytic activity.[23,24]

In this study, we prepared ZnO nanoparticles by annealing the products of zinc nitrate hexahydrate and sodium hydroxide at 700°C. The efficiency of ZnO nanoparticles in the photocatalytic degradation of 3-nitrophenol under ultraviolet irradiation was analyzed by UV-vis spectrophotometry.

Experimental

1. Chemicals and Instruments

Zinc nitrate hexahydrate [$Zn(NO_3)_2{\cdot}6H_2O$] and sodium hydroxide (NaOH) were obtained from Samchun Chemicals (Korea). Ethanol (C_2H_5OH) was obtained from Sigma-Aldrich, Inc. 3-Nitrophenol was supplied by Tae Jin Chemical. All chemicals were used directly without any further purification.

A hot-plate magnetic stirrer (MS-300HS) was used for stirring the solutions. The structure of the nanoparticles was examined by XRD (Bruker, D8 Advance). SEM (JEOL Ltd, JSM-6510) at an accelerating voltage of 0.5 to 30 kV was used to observe the surface of the nanoparticle samples. An electric furnace (Ajuon Heating Industry Co., Ltd) was used to heat the samples at 700°C for 2 h under atmosphere of inert argon gas. UV-vis spectroscopy (Shimazu UV-1691PC) with a wavelength range from 200 to 800 nm was used to evaluate the photo-degradation process. Photo-degradation of 3-nitrophenol was performed using a UV lamp (8 W, 254 nm/365 nm, Marne La Vallee-Cedex, France).

2. Preparation of ZnO nanoparticles

Each amount of (0.01 mole) zinc nitrate hexahydrate [$Zn(NO_3)_2{\cdot}6H_2O$] and (0.1 mole) sodium hydroxide [NaOH] were dissolved in a mixture of 6 mL deionized water and 15 mL ethanol. Then, the mixture of zinc nitrate hexahydrate and sodium hydroxide was stirred for 20 min. After 1 h of ultrasonic treatment, the ZnO nanoparticle precursor was fabricated. ZnO nanoparticles were then synthesized by annealing the ZnO precursor in an electric furnace at 700°C for 2 h under an atmosphere of inert argon gas.

3. Photocatalytic degradation of 3-nitrophenol with ZnO nanoparticles

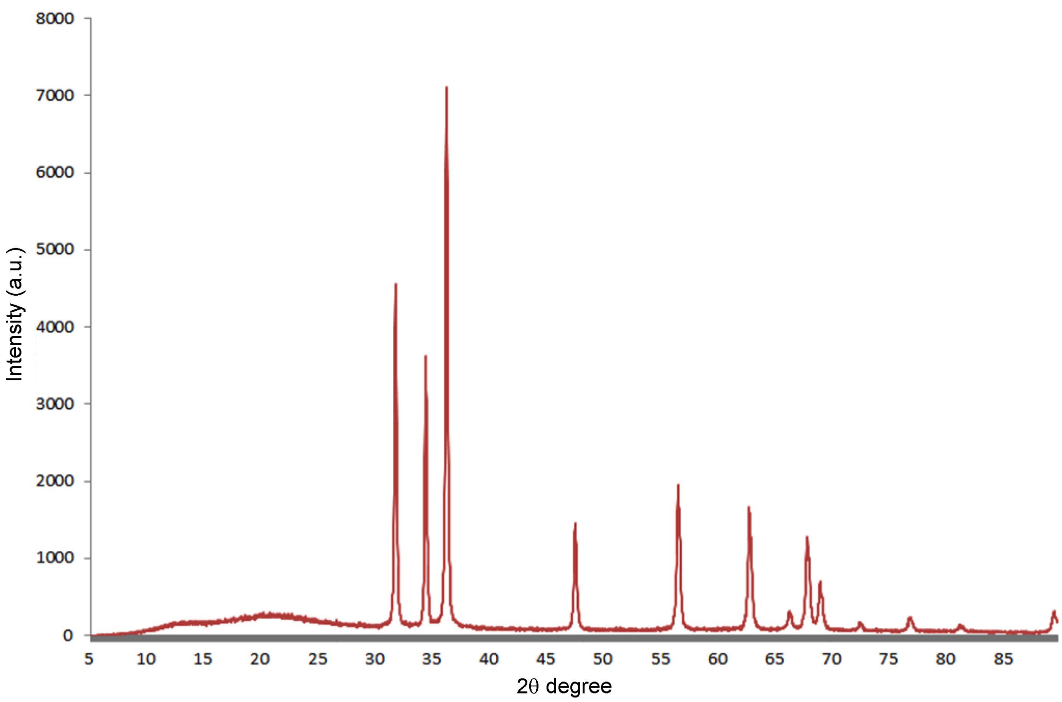

Figure 1. XRD pattern of ZnO nanoparticles.

The photocatalytic activity of ZnO nanoparticles was investigated by the degradation of 3-nitrophenol (3-NP) under ultraviolet irradiation. ZnO nanoparticles (5 mg) were added to a 10 mL 3-nitrophenol solution (0.05 mmol L^{-1}) in a glass vial. The suspension was left in the dark for 30 min to achieve adsorption-desorption equilibrium. Then, the glass vial was irradiated by UV-lamp at 254 nm at a distance of 1 cm. The photocatalytic degradation of 3-nitrophenol with ZnO nanoparticles as photocatalyst was recorded by an UV-vis spectrophotometer at 30 min intervals.

Results and Discussion

1. Crystal structure and morphology of ZnO nanoparticles

ZnO nanoparticles synthesized from zinc nitrate hexahydrate and sodium hydroxide were found to have good crystallinity and large surface areas. The crystal structure of the ZnO nanoparticles was examined by XRD in Figure 1. The XRD spectra showed peaks at 31.8°, 34.5°, 36.3°, 47.6°, 56.7°, 62.9°, 66.4°, 68.0°, 69.2°, 72.6° and 77.1° as 2θ values, which can be assigned to (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) ZnO nanoparticle crystal planes, respectively.[25] The sharp and significant peaks indicate that the synthesized ZnO nanoparticles have a small crystallite size. The morphological studies of the ZnO nanoparticles are displayed in Figure 2. Analysis of the SEM image showed that the ZnO nanoparticles have a porous structure and large surface area.

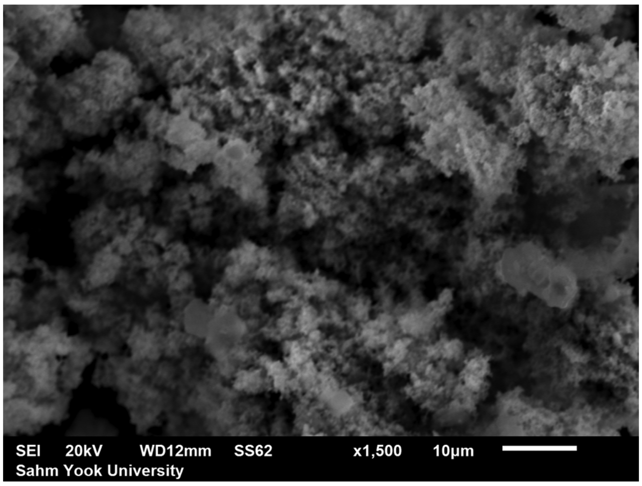

Figure 2. SEM image of ZnO nanoparticles.

2. Photocatalytic degradation of 3-nitrophenol with ZnO nanoparticles

The photocatalytic activity of the ZnO nanoparticles was investigated in the degradation of 3-nitrophenol under ultra-

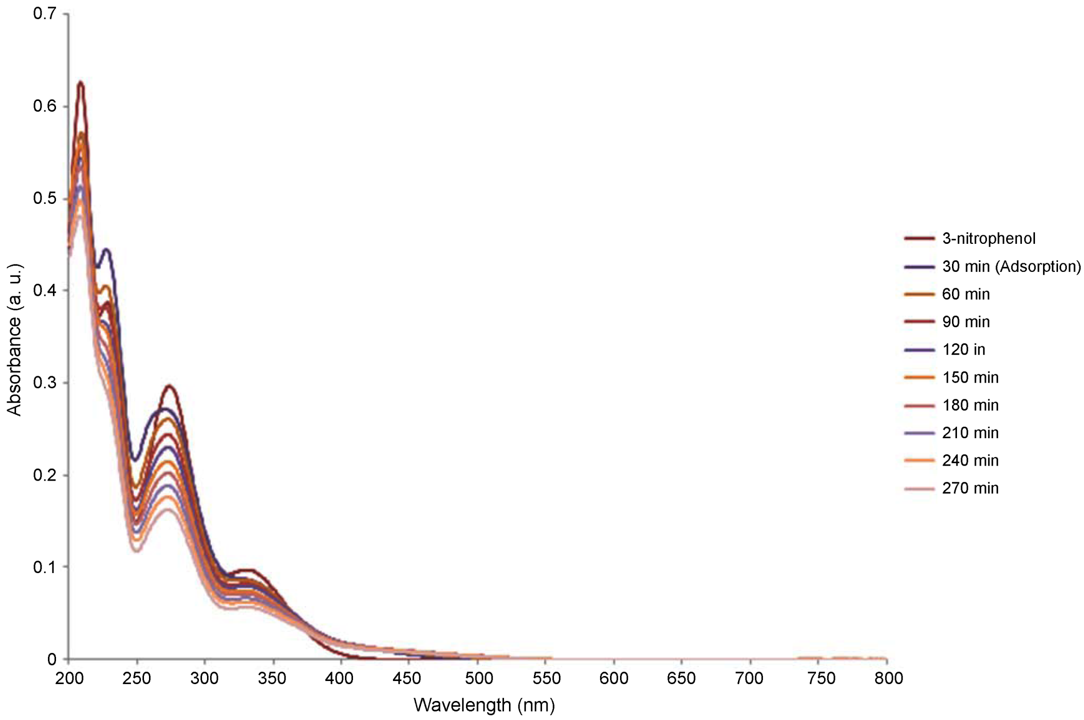

Figure 3. UV-vis spectrum of 3-nitrophenol photodegradation with ZnO nanoparticles as photocatalyst under 254 nm UV irradiation.

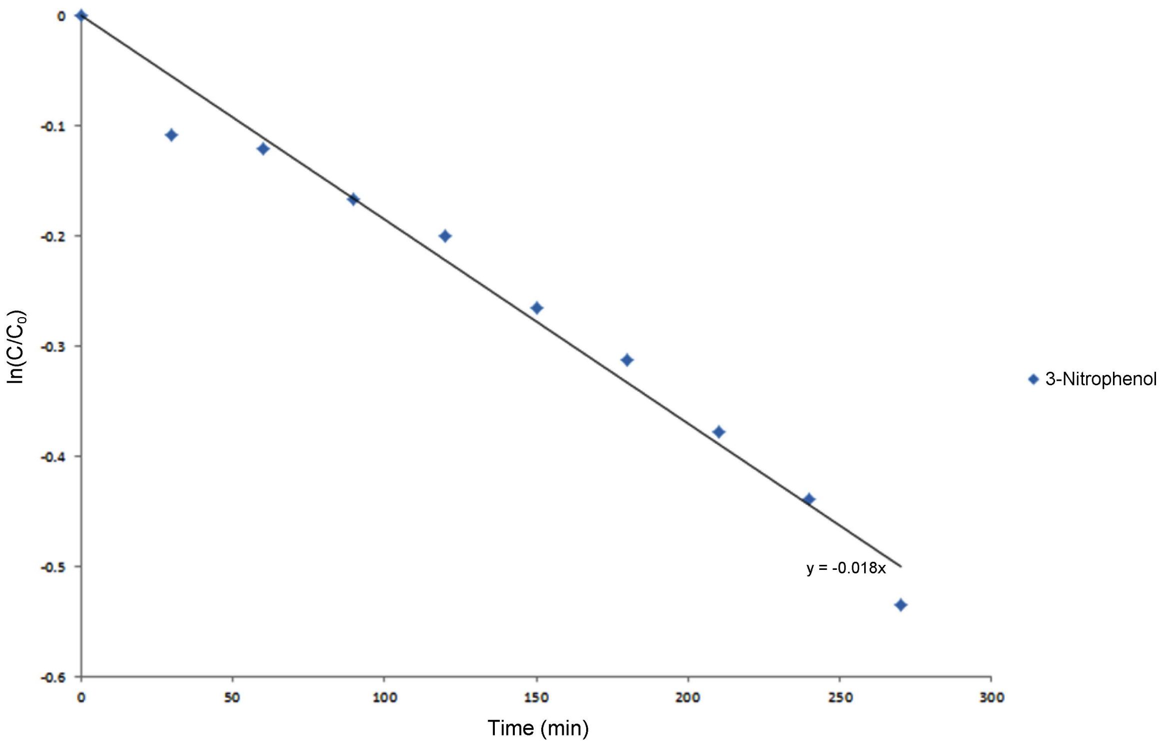

Figure 4. Kinetic study for photodegradation of 3-nitrophenol using ZnO nanoparticles as photocatalyst under 254 nm UV irradiation.

violet irradiation at 254 nm. Figure 3 shows the effect of the ZnO nanoparticles on the photocatalytic degradation of 3-nitrophenol. After the ZnO nanoparticles and 3-nitrophenol mixture achieved adsorption-desorption equilibrium, the reaction vial was irradiated by UV-lamp at 254 nm. With the increasing irradiation time, the color of the solution changed from deep yellow to light yellow, and the absorption intensity of 3-nitrophenol at 330 nm decreased, indicating the degradation. The kinetic data of the photocatalytic degradation of 3-nitrophenol was fitted to a pseudo-first order reaction rate model, which is shown in Figure 4.

Conclusion

In this study, we synthesized ZnO nanoparticles with a facile method, and impurities in ZnO nanoparticles were removed by washing and calcination at 700°C. The synthesized ZnO nanoparticles were determined to have good crystallinity and small crystallite size by XRD. The large surface area of the ZnO nanoparticles facilitated the effective photodegradation of 3-nitrophenol. Photocatalytic degradation of 3-nitrophenol with ZnO nanoparticles was also shown to follow a pseudo-first order reaction mechanism.

Acknowledgements

This study was supported by Sahmyook University research funding in Korea.

References

1. D. Mohan, A. Sarswat, V. K. Singh, M. A. Franco, and C. U. Pittman Jr., “Development of magnetic activated carbon from almond shells for trinitrophenol removal from water”, *Chem. Eng. J.*, **172**, 1111 (2011).
2. B. Zhao, G. Mele, I. Pio, J. Li, L. Palmisano, and G. Vasapollo, “Degradation of 4-nitrophenol (4-NP) using Fe-TiO_2 as a heterogeneous photo-Fenton catalyst”, *J. Hazard. Mater.*, **176**, 569 (2010).
3. M. S. Dieckmann and K. A. Gray, “A comparison of the degradation of 4-nitrophenol via direct and sensitized photocatalysis in TiO_2 slurries”, *Water Res.*, **30**, 1169 (1996).
4. S. U. Sonavane, M. B. Gawande, S. S. Deshpande, A. Venkataraman, and R. V. Jayaram, “Chemoselective transfer hydrogenation reactions over nanosized γ-Fe_2O_3 catalyst prepared by novel combustion route”, *Catal. Commun.*, **8**, 1803 (2007).
5. A. Santos, P. Yustos, S. Rodriguez, and F. G. Ochoa, “Wet oxi-

dation of phenol, cresols and nitrophenols catalyzed by activated carbon in acid and basic media", *Appl. Catal. B: Environ.*, **65**, 269 (2006).
6. G. Nakhla, S. Abuzaid, and S. Farooq, "Activated carbon adsorption of phenolics in oxic systems: Effect of pH and temperature variations", *Water Environ. Res.*, **66**, 842 (1994).
7. M. Maeda, A. Itoh, and Y. Kawase, "Kinetics for aerobic biological treatment of *o*-cresol containing wastewaters in a slurry bioreactor: biodegradation by utilizing waste activated sludge", *Biochem. Eng. J.*, **22**, 97 (2005).
8. C. J. Martino and P. E. Savage, "Oxidation and Thermolysis of Methoxy-, Nitro-, and Hydroxy-Substituted Phenols in Supercritical Water", *Ind. Eng. Chem. Res.*, **38**, 1784 (1999).
9. V. Maurino, C. Minero, E. Pelizzetti, P. Piccinini, N. Serpone, and H. Hidaka, "The fate of organic nitrogen under photocatalytic conditions: degradation of nitrophenols and aminophenols on irradiated TiO_2", *J. Photochem. Photobiol. A: Chem.*, **109**, 171 (1997).
10. D. A. Kazakov, V. V. Volkhin, K. Kaczmarski, Y. O. Gulenova, M. N. Obirina, and D. A. Rozhina, "Catalytic Ozonation of 4-Nitrophenol in the Presence of Magnetically Separable Titanium Dioxide-Magnetite Composite", *Euras. Chem. Technol. J.*, **17**, 309 (2015).
11. V. Augugliaro, L. Palmisano, M. Schiavello, and A. Sclafani, "Photocatalytic degradation of nitrophenols in aqueous titanium dioxide dispersion", *Appl. Catal.*, **69**, 323 (1991).
12. N. Daneshvar, M. A. Behnajady, and Y. Z. Asghar, "Photooxidative degradation of 4-nitrophenol (4-NP) in UV/H_2O_2 process: Influence of operational parameters and reaction mechanism", *J. Hazard. Mater. B*, **139**, 275 (2007).
13. N. Sobana, K. Selvam, and M. Swaminathan, "Optimization of photocatalytic degradation conditions of Direct Red 23 using nano-Ag doped TiO_2", *Sep. Purif. Technol.*, **62**, 648 (2008).
14. M. Sahiner, H. Ozay, O. Ozay, and N. Aktas, "A soft hydrogel reactor for cobal nanoparticle preparation and use in the reduction of nitrophenols", *Appl. Catal. B: Environ.*, **101**, 137 (2010).
15. D. M. Dotzauer, J. Dai, L. Sun, and M. L. Bruening, "Catalytic Membranes Prepared Using Layer-by-Layer Adsorption of Polyelectrolyte/Metal Nanoparticle Films in Porous Supports", *Nano Lett.*, **6**, 2268 (2006).
16. X. W. Zhang, Y. Y. Qu, W. L. Shen, J. W. Wang, H. J. Li, Z. J. Zhang, S. Z. Li, and J. T. Zhou, "Biogenic synthesis of gold nanoparticles by yeast Magnusiomyces ingens LH-F1 for catalytic reduction of nitrophenols", *Colloids Surf. A Physicochem. Eng. Asp.*, **497**, 280 (2016).
17. M. S. Dieckmann and K. A. Gray, "A comparison of the degradation of 4-nitrophenol via direct and sensitized photocatalysis in TiO_2 slurries", *Wat. Res.*, **30**, 1169 (1996).
18. B. Divband, M. Khatamian, G. R. K. Eslamian, and M. Darbandi, "Synthesis of Ag/ZnO nanostructures by different methods and investigation of their photocatalytic efficiency for 4-nitrophenol degradation", *Appl. Surf. Sci.*, **284**, 80 (2013).
19. K. M. Parida and S. Parija, "Photocatalytic degradation of phenol under solar radiation using microwave irradiated zinc oxide", *Sol. Energy*, **80**, 1048 (2006).
20. D. W. Chen and A. K. Ray, "Photodegradation kinetics of 4-nitrophenol in TiO_2 suspension", *Wat. Res.*, **32**, 3223 (1998).
21. R. S. Parra, I. H. Perez, E. M. Palacios, J. P. P. Orozco, A. Sampieri, D. V. Avella, A. E. J. Gonzalez, and R. G. Tapia, "Photodegradation of Phenol, 2-Chlorophenol and *o*-Cresol by Iron Oxide Nanoparticles", *Nanosci. Nanotechnol. Asia*, **1**, 31 (2011).
22. F. Peng, H. J. Wang, H. Yu, and S. H. Chen, "Preparation of aluminum foil-supported nano-sized ZnO thin films and its photocatalytic degradation to phenol under visible light irradiation", *Mater. Res. Bull.*, **41**, 2123 (2006).
23. N. G. Shimpi, S. Jain, N. Karmakar, A. Shah, D. C. Kothari, and S. Mishra, "Synthesis of ZnO nanopencils using wet chemical method and its investigation as LPG sensor", *Appl. Surf. Sci.*, **390**, 17 (2016).
24. S. K. Pardeshi and A. B. Patil, "A simple route for photocatalytic degradation of phenol in aqueous zinc oxide suspension using solar energy", *Sol. Energy*, **82**, 700 (2008).
25. C. Q. Zhu, B. Lu, Q. Su, E. Q. Xie, and W. Lan, "A simple method for the preparation of hollow ZnO nanospheres for use as a high performance photocatalyst", *Nanoscale*, **4**, 3060 (2012).