CHEMIJA. 2014. Vol. 25. No. 1. P. 1–4

Different silver-modified zinc oxides for photocatalytic degradation of imidacloprid

Zsigmond Papp*

Department of Chemistry, Biochemistry and Environmental Protection, Faculty of Sciences, University of Novi Sad, Trg Dositeja Obradovića 3, 21000 Novi Sad, Serbia

Synthesis, scanning electron microscopic / energy dispersive spectrometric characterization and photocatalytic properties of two different silver-modified zinc oxides are described. Both catalyst types were synthesized from pure zinc oxide powder and an aqueous solution of silver nitrate in the presence of solar light. The first type was prepared by the photoreduction of silver ions on the zinc oxide surface in the absence of target molecules (imidacloprid), the second one was prepared in their presence – in situ. The photocatalytic properties of the obtained catalysts were compared with those of the pure zinc oxide. The catalyst obtained in situ in the presence of imidacloprid showed the highest activity.

Key words: silver-modified zinc oxide, photocatalysis, neonicotinoid insecticide, SEM/EDS

INTRODUCTION

The photocatalytic efficiency of semiconductor nanoparticles is often limited by the quick recombination of the photogenerated charge carriers [1, 2]. One of the mostly used ways to overcome these limitations is deposition of noble metals on the semiconductor surface, which prevents the recombination of the electron-hole pairs and consequently increases its photocatalytic activity [3–5].

Neonicotinoid insecticides represent the most important chemical class of insecticides introduced to the global market since the synthetic pyrethroids [6]. Massive application of neonicotinoids also requires efficient methods for their removal from the environment. While TiO_2-based catalytic systems are broadly applied for the photocatalytic degradation of neonicotinoid insecticides [7–12], there are only few examples of the use of ZnO-based systems [11, 13, 14]. To the best of my knowledge there are no publications dealing with noble metal-modified ZnOs for the photocatalytic degradation of neonicotinoids.

Among noble metal-modified ZnOs, silver-modified ones enjoy wide popularity in the photocatalytic removal of different organic pollutants [15–26], mostly organic dyes. One of the most elegant ways of producing these catalysts is by photoreduction [27–29] of silver(I) ions on the ZnO surface.

In this work two different synthetic approaches are presented for obtaining silver modified ZnOs (Ag/ZnOs) for the photocatalytic removal of imidacloprid (Fig. 1) neonicotinoid insecticide. The first type (Ag/ZnO/1) was prepared by the photoreduction of silver(I) ions on the ZnO surface in the absence of target molecules (imidacloprid), the second one (Ag/ZnO/2) was prepared in their presence – in situ. The photocatalytic features of Ag/ZnOs were compared with those of unmodified ZnO. Scanning electron microscopy / energy dispersive spectrometry (SEM/EDS) was applied for the morphological, structural and elemental characterization of the modified catalysts.

* Corresponding author. E-mail: zsigmond.papp@dh.uns.ac.rs

EXPERIMENTAL

Catalyst preparation

Both silver modified catalysts were prepared from pure ZnO powder (Kemika, Croatia, p. a., min. 99%) and an aqueous solution of $AgNO_3$ (Poch, Poland, p. a.). Ag/ZnO/1: The oxide was suspended in 10 cm^3 of 0.01 mol/dm^3 $AgNO_3$ solution and insolated using natural solar light for 3 hours before the photocatalytic experiment. Later, 50 cm^3 of 2.35×10^{-4} mol/dm^3 imidacloprid (obtained from liquid commercial formulation Macho 200 SL, Hemovet, Serbia; the procedure is described below) solution was added. After proper mixing the suspension was insolated again using natural solar light. Ag/ZnO/2: The oxide was suspended in 10 cm^3 of 0.01 mol/dm^3 $AgNO_3$ solution in the dark. Before the photocatalytic experiment 50 cm^3 of 2.35×10^{-4} mol/dm^3 imidacloprid solution was added (also in dark), mixed properly, and later insolated using natural solar light.

Extraction of imidacloprid

Imidacloprid (solubility in water at 20 °C is 0.61 g/dm^3 [30]) was obtained from commercial formulation Macho 200 SL. In the first step 50 cm^3 of this solution (containing ~10 g of imidacloprid) was slowly poured into cold (~4 °C) doubly distilled water. The formed white–pale yellow crystals were filtered through quantitative filter paper and washed with 250 cm^3 of cold water. The obtained crystals were air dried at 30 °C. The UV absorption spectra (200–400 nm range, pH 7.0) of imidacloprid obtained were not distinguishable from the spectra of the commercially available analytical standard (Sigma-Aldrich Laborchemikalien GmbH, Germany; PESTANAL®; 99.9%).

Photodegradation

60 cm^3 of solution with or without a catalyst were subjected to natural solar irradiation for 3 hours. Control samples were kept in the dark. All solutions were mixed few times during the experiment to minimize sedimentation. All experiments were done in duplicate.

Spectrophotometry

Spectrophotometric measurements were performed on a PG Instruments T80+ UV–visible double-beam spectrophotometer (PG Instruments, United Kingdom) using quartz cuvettes with 1 cm path lenth. The samples for the analysis were filtered through appropriate membrane filters. The degradation of imidacloprid was monitored at its most intensive absorption maxima at 270 nm. The degradation efficiency (%) was calculated using the following equation:

$$Degradation\ efficiency = [(A_0 - A_t) / A_0] \times 100,$$

where A_0 represents the intial absorbance and A_t is the absorbance at time, t.

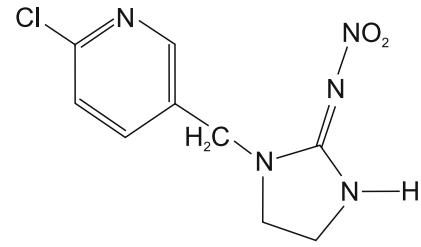

Fig. 1. Structural formula of imidacloprid

SEM/EDS measurements

Surface characterization of Ag/ZnO/2 was done with the aid of a JSM-6460LV electron microscope (Jeol, Japan) and an INCAx-sight EDS detector (Oxford Instruments, United Kingdom). After its use in the photodegradation experiment, Ag/ZnO/2 was filtered through quantitative filter paper, washed with doubly distilled water, and air dried for two days. The surface elemental analysis of the catalyst was done without any pretreatment, while the structure and morphology were investigated after gold evaporation to the surface of the investigated sample using a BAL-TEC SCD-005 (Bal-Tec AG, Lichtenstein) sputter coater (working time, 90 s; used current, 30 mA; working distance, 50 mm).

RESULTS AND DISCUSSION

The efficiency of unmodified ZnO and synthesized Ag/ZnOs was tested in the solar photocatalytic degradation of imidacloprid and clear differences were observed in the disappearance rate of the target compound. Although ZnO showed quite high activity, both synthesized silver modified catalysts surpassed its efficiency.

After one hour of photodegradation the absorbance of imidacloprid (together with its degradation intermediates) at 270 nm decreased by about 37.4% in case of ZnO, while Ag/ZnO/1 and Ag/ZnO/2 resulted in a decrease of 47.3 and 66.3%, respectively (Fig. 2, C–E). During the investigated period no photolytic degradation was observed (Fig. 2, B). The solution of imidacloprid in the dark also remained unchanged (Fig. 2, A).

The most efficient photocatalyst (Ag/ZnO/2) was subjected to further physicochemical investigation. Figure 3 shows the morphological, structural and elemental characterization of Ag/ZnO/2 after its use in the photocatalytic experiment. Typical micrographs of the catalyst taken under different magnifications (Fig. 3A, B) clearly show agglomerates consisting of smaller particles with the size mostly in the 80–500 nm range. The EDS analysis of the catalyst showed the expected ratio of zinc and oxygen for pure ZnO together with about 4.7% (w/w) of silver. The presence of other elements was negligible. Separate silver particles with the size comparable to the size of ZnO particles were not identified in the sample, therefore it is assumed that silver is present on the surface of ZnO particles in the form of highly dispersed nanoparticles or a thin film.

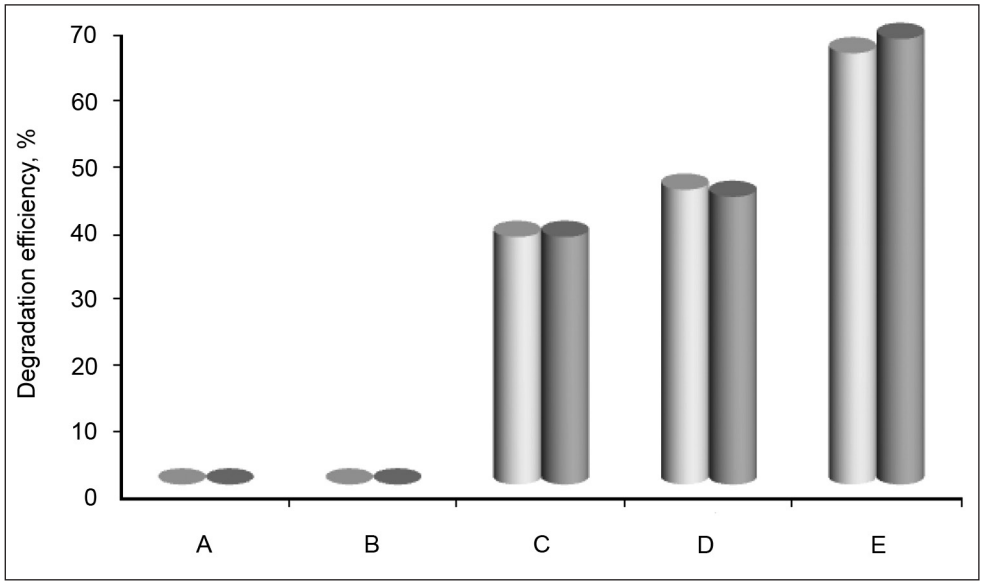

Fig. 2. Efficiency of different procedures of imidacloprid photodegradation after 1 hour: without a catalyst / dark regime (A), photolysis (B), unmodified ZnO (C), Ag/ZnO/1 (D), Ag/ZnO/2 (E)

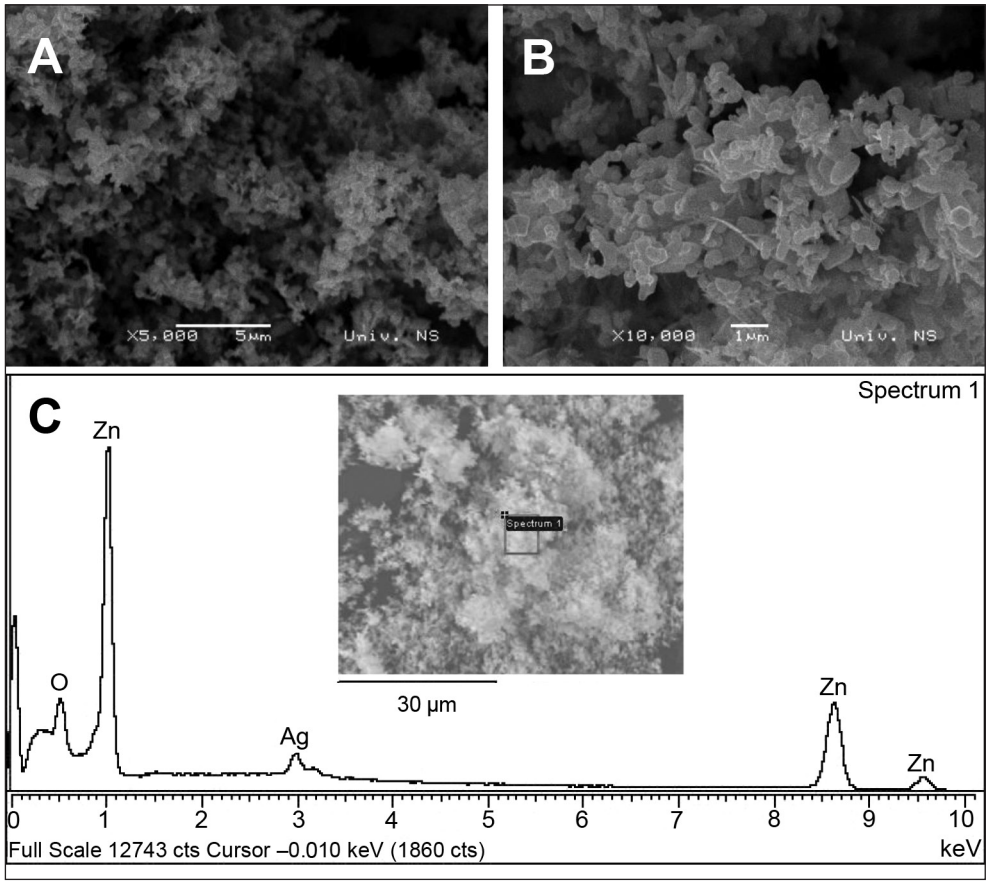

Fig. 3. SEM micrographs of the Ag/ZnO/2 sample under different magnifications (×5,000 (A), ×10,000 (B)) and EDS spectra from its representative surface area (C)

Visual assessment of the catalytic systems during the photodegradation showed that the suspension with Ag/ZnO/1 had much darker color (dark grey) in comparison with Ag/ZnO/2 containing one (slight grey) as a result of very intense photoreduction of silver(I) ions on the ZnO surface before its application in the photocatalytic experiment. Too high amount of silver in Ag/ZnO/1 is probably the reason of its slightly reduced photocatalytic efficiency.

CONCLUSIONS

New silver modified zinc oxides (Ag/ZnOs) have been prepared and successfully applied in the solar photodegradation of imidacloprid insecticide. The photocatalyst prepared by the photodeposition of silver(I) ions on the ZnO surface in the presence of the target compound (Ag/ZnO/2) showed the highest activity in comparison with unmodified ZnO and the catalyst prepared by photodeposition in the absence of target molecules. This catalyst was subjected to morphological and structural characterization using SEM. The presence of silver on its surface was successfully confirmed with the aid of EDS.

The applied in situ surface modification of the catalyst in the presence of the target compound (Ag/ZnO/2–imidacloprid system) greatly simplified the photocatalytic procedure and at the same time enhanced the catalytic efficiency. For the determination of the exact mechanism of interaction between the semiconductor particles, modifier and target compound, additional thoroughgoing experiments are needed. In any case, this work broadens the field of preparation and application of noble metal-modified semiconductor catalysts for the solar photodegradation of organic pollutants.

ACKNOWLEDGEMENTS

The financial support of the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project Nos. ON172059 and ON172012) is gratefully acknowledged. The author would also like to thank Mr. Miloš Bokorov for his help in this research.

Received 28 October 2013
Accepted 14 November 2013

References

1. P. V. Kamat, *Chem. Rev.*, **93**, 267 (1993).
2. G. Rothenberger, J. Moser, M. Grätzel, N. Serpone, D. K. Sharma, *J. Am. Chem. Soc.*, **107**, 8054 (1985).
3. K. Rajeshwar, N. R. de Tacconi, C. R. Chenthamarakshan, *Chem. Mater.*, **13**, 2765 (2001).
4. P. V. Kamat, *J. Phys. Chem. B*, **106**, 7729 (2002).
5. P. V. Kamat, *Pure Appl. Chem.*, **74**, 1693 (2002).
6. P. Jeschke, R. Nauen, *J. Agric. Food Chem.,* **64**, 1084 (2008).
7. A. Agüera, E. Almansa, S. Malato, M. I. Maldonado, A. R. Fernández-Alba, *Analusis*, **26**, 245 (1998).
8. S. Malato, J. Caceres, A. Agüera, et al., *Environ. Sci. Technol.*, **35**, 4359 (2001).
9. N. M. Mahmoodi, M. Arami, N. Y. Limaee, K. Gharanjig, *J. Hazard. Mater.*, **145**, 65 (2007).
10. U. Černigoj, U. L. Štangar, P. Trebše, *Appl. Catal. B: Environ.*, **75**, 231 (2007).
11. V. Kitsiou, N. Filippidis, D. Mantzavinos, I. Poulios, *Appl. Catal. B: Environ.*, **86**, 27 (2009).
12. R. Žabar, T. Komel, J. Fabjan, M. B. Kralj, P. Trebše, *Chemosphere*, **89**, 293 (2012).
13. S. Sathiyanarayanan, P. E. Ravi, A. Ramesh, *Open Catal. J.*, **2**, 24 (2009).
14. B. F. Abramović, N. Banić, J. B. Krstić, *Ind. Eng. Chem. Res.*, **52**, 5040 (2013).
15. L. Wang, Q. Hu, Z. Li, J. Guo, Y. Li, *Mater. Lett.*, **79**, 277 (2012).
16. K. Thongsuriwong, P. Amornpitoksuk, S. Suwanboon, *J. Sol-Gel Sci. Technol.*, **62**, 304 (2012).
17. A. A. Ashkarran, *Appl. Phys. A*, **107**, 401 (2012).
18. T.-J. Whang, M.-T. Hsieh, H.-H. Chen, *Appl. Surf. Sci.*, **258**, 2796 (2012).
19. D. Zhang, F. Zeng, *Res. Chem. Intermed.*, **36**, 1055 (2010).
20. Y. Lai, M. Meng, Y. Yu, *Appl. Catal. B: Environ.*, **100**, 491 (2010).
21. J. Xie, Q. Wu, *Mater. Lett.*, **64**, 389 (2010).
22. R. Georgekutty, M. K. Seery, S. C. Pillai, *J. Phys. Chem. C*, **112**, 13563 (2008).
23. J. Wang, X. M. Fan, Z. W. Zhou, K. Tian, *Mater. Sci. Eng. B*, **176**, 978 (2011).
24. C. A. K. Gouvêa, F. Wypych, S. G. Morales, N. Durán, P. Peralta-Zamora, *Chemosphere*, **40**, 427 (2000).
25. J. Liqiang, W. Dejun, W. Baiqi, et al., *J. Mol. Catal. A: Chem.*, **244**, 193 (2006).
26. P. V. Korake, R. Sridharkrishna, P. P. Hankare, K. M. Garadkar, *Toxicol. Environ. Chem.*, **94**, 1075 (2012).
27. G. Tamman, Z. *Anorg. Chem.*, **114**, 151 (1920).
28. P. D. Fleischauer, H. K. Alan Kan, J. R. Shepherd, *J. Am. Chem. Soc.*, **94**, 283 (1972).
29. H. Hada, H. Tanemura, Y. Yonezawa, *Bull. Chem. Soc. Jpn.*, **51**, 3154 (1978).
30. C. D. S. Tomlin (ed.), *The Pesticide Manual: A World Compendium*, 15th edn., British Crop Protection Council, Farnham, Surrey, UK (2009).

Zsigmond Papp

SIDABRU MODIFIKUOTI CINKO OKSIDO MĖGINIAI FOTOKATALIZINEI IMIDAKLOPRIDO DESTRUKCIJAI

S a n t r a u k a

Aprašyta dviejų skirtingų sidabru modifikuotų cinko oksido mėginių sintezė ir pateiktos charakteristikos, atliktos fizikocheminiais metodais. Abu mėginiai buvo susintetinti iš gryno cinko oksido miltelių ir sidabro nitrato vandeninio tirpalo veikiant saulės šviesai. Vienas mėginys gautas nesant, o kitas – esant reakcinėje terpėje imidakloprido. Pateiktos palyginamosios abiejų mėginių charakteristikos.