Photocatalytic degradation of sulfur mustard over NiO-ZnO/TiO_2 composites

Nicoleta Petrea,[a] Răzvan Petre,[a] Constantin Toader,[a] Florentina Neațu,[b] Mihaela Florea,[b]
Laura E. Abramiuc,[b] Cristian M. Teodorescu,[b] Vasile Șomoghi,[c] Ștefan Neațu[b,c,*]
[a]*Scientific Research Centre for CBRN Defense and Ecology, 225 Oltenitei Road, 041309 Bucharest, Romania*
[b]*National Institute of Materials Physics, 405A Atomistilor Street, 077215 Magurele, Romania*
[c]*SC STIMPEX SA, 46-48 Nicolae Teclu, 032368 Bucharest, Romania*
**Corresponding author: +40 21 369 01 77, stefan.neatu@infim.ro*

Abstract: The photocatalytic degradation of sulfur mustard was investigated over NiO-ZnO/TiO_2 materials under UV light irradiation at a high concentration of blister agent of 0.77 wt. %. Half of sulfur mustard was decomposed in less than 20 minutes from the start of the reaction over 50 wt. % NiO-ZnO/TiO_2 (9:1), which was the best photocatalytic system. The catalytic tests performed on a wide range of contaminated surfaces confirm the activity and stability of the investigated photocatalytic systems, these materials being suitable from economical point of view to be used in the formulation of a possible decomposition kit with military applicability.

Keywords: p-n junction, heterojunction photocatalysts, sulfur mustard degradation.

1. Introduction

Of all known chemical warfare agents (CWA) produced so far, sulfur mustard (bis(2-chloroethyl)sulfide or yperite) is, in terms of quantity, the most used chemical weapon in military conflicts, the starting point being the Belgian town Ypres during the First World War.[1] Although the decomposition of sulfur mustard is a chemical process that is hard to be achieved, it is believed that the decontaminant which could efficiently destroy yperite can also be used in the decontamination process of nearly any other CWA.[2] One feasible technique that can be applied for the efficient degradation of sulfur mustard is photocatalysis.[3] In recent years, photocatalysis has been intensively applied in the mineralization of a wide range of toxic compounds and the efficiency of the oxidation process of sulfur mustard and its surrogates has been demonstrated, especially on TiO_2-based photocatalysts.[4] In almost all the photocatalytic processes reported so far, the decontaminant was mainly a semiconductor, not doped and/or doped with metal or semimetal ions, while the coupling of the various semiconductors was sparingly studied. In this regard, it is well documented that the coupling of p-type semiconductors with other n-type semiconductors forms a p-n junction, which leads to a significant improvement in photoactivity due to an efficient charge separation process.[5-7] In view of these findings and the fact that no photocatalytic results on this particular compounds are yet reported, it will be interesting to investigate the photocatalytic behavior of such a composite consisting of a p-type semiconductor, such as NiO, and the n-type semiconductors well studied TiO_2 Evonik P25 and ZnO in the degradation of a CWA, such as sulfur mustard.

2. Experimental

In this study, the adopted synthetic approach implies the deposition-precipitation of the Ni and Zn nanoparticles onto the surface of TiO_2 Evonik P25. In this way, several photocatalysts with different Ni:Zn ratios (1:1, 3:1, 6:1 and 9:1) were synthesized by simply adding TiO_2 Evonik P25 to solutions containing calculated amounts of Ni and Zn nanoparticles to reach a total metal loading of 50 wt. %.[8] The obtained solid samples were later on filtered, washed, dried, thermally stabilized and reduced under H_2 atmosphere at 350 °C for 2h. The samples properties were further investigated by using different characterization techniques, such as: DR-UV-Vis spectroscopy, powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The sulfur mustard degradation reaction has been performed by putting in contact 100 μL of toxic compound solution with 20 mg of photocatalyst. The evolution of the reaction was followed by extracting the suspension with dichloromethane after 5, 20, 30 minutes and 120 of UV light irradiation, concentrating the resulting extracts and analyzing by using a gas chromatograph coupled with a mass spectrometer.

3. Results and discussion

NiO-ZnO/TiO_2 photocatalysts present interesting properties. For instance, the XRD patterns show besides the characteristic diffraction lines of TiO_2 anatase and rutile, the presence of the metallic Ni. The presence of NiO cannot be ruled out, due to the fact that the most intense diffraction lines characteristic to cubic NiO are superposing the one of anatase. However, the presence of NiO and ZnO on the surface of TiO_2 can be envisaged from XPS spectrum. Figure 1 presents the typical PXRD pattern and XPS spectrum of the best NiO-ZnO/TiO_2 photocatalysts used in this work.

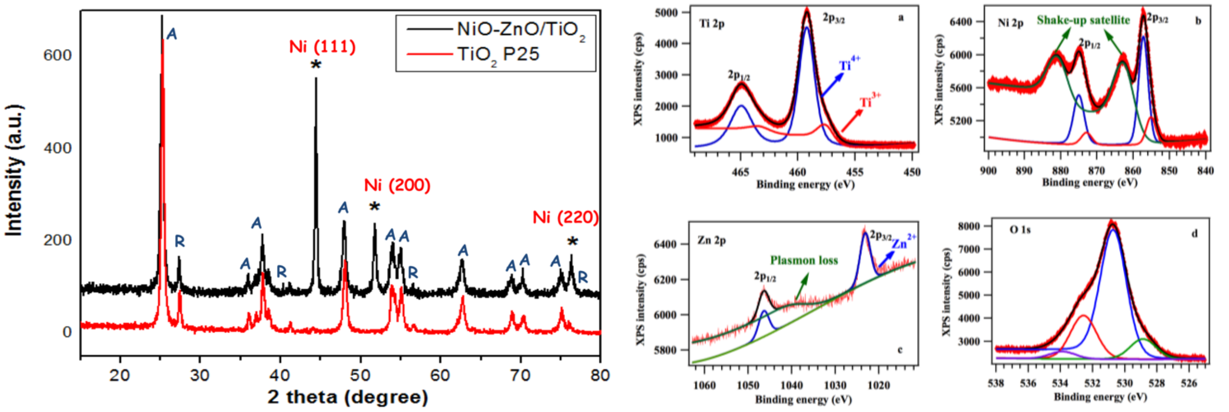

Figure 1. Left: The XRD patterns of the TiO_2 Evonik P25 (red) and the NiO-ZnO/TiO_2 (9:1) photocatalyst (black) and their corresponding phase assignments (A=anatase and R=rutile). The Ni metallic crystallographic phases are presented as *. **Right:** The XP spectrum of the NiO-ZnO/TiO_2 (9:1) photocatalysts in the Ti 2p, Ni 2p, Zn 2p and O 1s region, respectively.

The results obtained in the photocatalytic degradation of sulfur mustard under UV light irradiation showed that NiO-ZnO/TiO_2 materials possess good activity, the (9:1) sample being able to destroy 50% of yperite in just 20 minutes of light exposure, while the parent TiO_2 photocatalyst can reach a yield of degradation of around 20% only after 120 minutes.

4. Conclusions

The data presented in this study show that we have obtained efficient photocatalysts for the degradation of sulfur mustard. In the presence of these photocatalysts, the degradation rate was higher than on the parent TiO_2 Evonik P25 catalyst, in all the cases. The results open new opportunities in the preparation of very active materials for CWA degradation based on the optimization of three-component structures.

Acknowledgements: This work was supported by the follow grants of the Romanian National Authority for Scientific Research, CNDI–UEFISCDI project numbers: PN-II-PT-PCCA-2013-4-1468, PN-III-P2-2.1-PTE-2016-0120, PN-III-P1-1.2-PCCDI 2017-0637.

References

1. J.P. Robinson, M. Leitenberg, The Problem of Chemical and Biological Warfare, Vol. 1, Almquist & Wiksells, Stockholm, 1971
2. S. Neatu, B. Cojocaru, V.I. Parvulescu, V. Somoghi, M. Alvaro, H. Garcia, J. Mater. Chem. 20 (2010) 4050.
3. S. Neatu, V.I. Parvulescu, G. Epure, E. Preda, V. Somoghi, A. Damin, S. Bordiga, A. Zecchina, Phys. Chem. Chem. Phys. 10 (2008) 6562.
4. B. M. Smith, Chem. Soc. Rev. 37 (2008) 470.
5. Z. Zhang, C. Shao, X. Li, C. Wang, M. Zhang, and Y. Liu, ACS Appl. Mater. Interfaces 2 (2010) 2915.
6. H. He, P. Xiao, M. Zhou, Y. Zhang, Q. Lou, and X. Dong, Int. J. Hydrogen Energy 37 (2012) 4967.
7. M. Wang, L. Sun, Z. Lin, J. Cai, K. Xie, and C. Lin, Energy Environ. Sci. 6 (2013) 1211.
8. S. Neatu, F. Neatu, L.E. Abramiuc, M. Florea, C.M. Teodorescu, unpublished results.