J | P | S | T Journal of Inttp://jpst.irost.ir Journal of Particle Science and Technology IROST

X-Shaped Thallium oxide nanostructures as a high performance photocatalyst for degradation of Cephalexin

Arezo Mohammadkhani¹, Azar Bagheri GH^{1,*}, Saeed Rayati²

¹ Department of Chemistry, Central Tehran Branch, Islamic Azad University, Tehran, Iran ² Department of Chemistry, K. N. Toosi University of Technology, Tehran, Iran

HIGHLIGHTS

GRAPHICAL ABSTRACT

- Thallium oxide nanopartilces were synthesized by a simple coprecipitation method and used as degradartion photocatalyst.
- The diffraction pattern and FESEM of the prepared Tl₂O₃ nanoparticles showed the X-shaped morphology.
- Cephalexin (CPX) has been degradated upto 97% after 15 min in the presence of Tl_2O_3 photocatalyst.



ARTICLE INFO

Article history: Received 14 May 2019 Revised 2 December 2019 Accepted 25 December 2019

Keywords: Tl₂O₃ Cephalexin Photocatalytic activity Band gap Co-precipitation method

ABSTRACT

In this study, we present an approach to synthesize Tl_2O_3 nanoparticles using a simple co-precipitation method that leads to the formation of X-shaped particles. The sample was characterized by XRD measurements, field emission scanning electron microscopy (FESEM), diffuse reflectance spectroscopy, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FT-IR), and ultraviolet-visible (UV-VIS). The absorption spectrum of the sample showed that the optical band gap was 3.5 eV. The prepared photocatalyst was used in the photocatalytic degradation of Cephalexin (CPX) using irradiation, and the optimum parameters that were obtained were 0.2 g.L⁻¹ of the photocatalyst at pH 5.5 and an irradiation time of 15 minutes.

1. Introduction

The wide application of antibiotics in human and veterinary medicine, has led to large-scale dissemination of refractory and even toxic pollutants in the environment. In many countries, a multitude of extremely resistant antibiotics have been found in treated sewage, industrial effluent, the aquatic environment, and even in drinking water. They are extremely resistant to biological degradation processes; because of their continuous input, they could remain in the environment for a long time. Their presence in the environment is considered dangerous in both low and high concentrations. Cephalexin, as one of the most popular antibiotics, is produced commercially in high quantities. Nowadays this drug is ubiquitously present in the aquatic environment due to its resistance to biodegradation. There are very few studies have been published on the photocatalytic degradation of CPX using suspension photocatalysts.

Recently, a variety of treatment methods, such as the advanced oxidation processes (AOPs) [1-2], anaerobic treatment [3], and powdered activated carbon adsorption, etc. [4], have been suggested for the treatment of most industrial effluents containing toxic organic chemicals.

 Tl_2O_3 is a metal oxide with high conductivity and a degenerate *n*-type semiconductor with a band gap of 1.4 eV, which has the potential for use in solar cells [5]. Thallium (III) oxide is a highly insoluble thermally stable thallium source suitable for glass, optic, and ceramic applications. Therefore, it is very important to be able to fabricate these nanoparticles using a very simple method. Due to the high solubility of thallium hydroxide in water and methanol, nano thallium oxide synthesis is difficult. Thus, there are only a few reports on the synthesis of nano-sized Tl_2O_3 using thermal decomposition [6], electrodeposition [7], and sonochemical [8] methods.

Thus, in this study we has examined the optimal conditions of degradation efficiency of the synthesized photocatalyst (Tl_2O_3 nanoparticles) in terms of CPX removal percentage from water.

2. Experimental

2.1. Materials

Thallium acetate (99.9%, Sigma Co.) and ethanol (99.9%, Sigma Co.) were used as received without

further purification. Other compounds used were prepared from ingredients obtained from the MERCK Company.

2.2. Apparatus

For the UV/photocatalytic process, irradiation was performed in a 0.2 L batch photoreactor equipped with four mercury lamps, Philips 8W (UV-C) (Fig.1). Phase identification of the fabricated sample was carried out by an Holland Philips X-ray diffraction CuK_{α} (λ = 1.5417 Å) in the radiation range of 20°-80°. A Field emission scanning electron micrograph (FESEM) from Holland Philips XL30 microscope was used to observe the morphology and elemental analysis of the sample. Diffuse reflectance spectroscopy (DRS) was recorded on a Shimadzu UV-2550 UV-visible spectrophotometer. X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific) was obtained with a monochromatic AlK_a radiation source. The presence of surface functional groups in the prepared samples was analyzed by FT-IR spectrum recorded using a Perkin Elmer FT-IR spectrometer.

2.3. Preparation of Tl_2O_3 nanostructures

3.3 mmol of KOH was dissolved in 36 ml distilled water under stirring. Then, 3 mmol of the template, hexamethylenetetramine, was added to the solution. Next, Thallium acetate (3 mmol) was added to the mixture and the mixture was refluxed for 3 h at 110 °C. After 2 week, the precipitate was collected by filtration and washed with distilled water and ethanol several



Fig. 1. Schematic diagram of the batch photocatalytic reactor.

(b)

times. Tl_2O_3 was obtained by centrifugation and drying of precipitate at room temperature. Lastly, the Tl_2O_3 nanoparticle was obtained via a controlled calcination process using a muffle furnace for 4h at 450 °C.

2.4. Photocatalytic activity measurement

Photocatalytic properties of the prepared Tl_2O_3 nanoparticles were evaluated by the degradation of a 20 mL CPX aqueous solution (50 fold dilution of the original solution as the optimum concentration) to obtain a suspension containing 0.2 g.L⁻¹ of the photocatalyst. During the reaction, the adsorbed CPX was sampled at regular intervals and the drug concentration was monitored by measuring the absorbance of the solution with a UV-Vis spectrophotometer.

3. Results and Discussion

3.1. Characterization of the photocatalyst

Fig. 2 provides a typical XRD pattern of product obtained from the co-precipitation method in an aqueous solution. All reflection peaks of the XRD pattern of Tl_2O_3 nanoparticles indexed well to the cubic phase of Tl_2O_3 . These peaks can be indexed as (211), (222), (400), (411), (332), (510), (440), (532), (622), (631), and (444) diffraction lines with space group of cubic (JCPDS card No. 05-0584). No other crystalline phases were detected.

The surface morphology of the prepared pure Tl_2O_3 nanoparticles was studied using FESEM (Fig. 3). According to FESEM images of the Tl_2O_3 nanoparticles,



Fig. 2. TXRD pattern of the synthesized Tl₂O₃ nanoparticles.

the product was mainly composed of a large amount of X-like nanoparticles.

Fig. 4 shows the FT-IR spectrum of the Tl_2O_3 nanostructure. The absorption bands in the range of 500-1450 cm⁻¹ can be attributed to the stretching and bending modes of Tl–O, and the weak band at about 3190 cm⁻¹ can probably be attributed to the presence of water in the KBr matrix.

The measured binding energies (BEs) of T14f7/2, upon correction by the C_{1s} peak at 284.54 eV, are centered at 116.59 and 119.1 eV. These values are assigned to oxide species Tl³⁺ (i.e., Tl₂O₃) and Tl⁺ (i.e., Tl₂O), respectively, in good agreement with the literature data [9,10]. The O_{1s} peak is slightly asymmetric tailing on the high binding energy side (Fig. 5), which might be attributed to hydroxyl groups at the outermost surface as well as to adsorbed water from air moisture. The detailed analysis of the O_{1s} region of the thallium oxide indicates the presence of contributions at 531.68 (OL) and 532.80 (OH) eV, which are assigned to O₂, OH⁻,



Fig. 3. FESEM images of the synthesized Tl₂O₃ nanoparticles.



Fig. 4. FT-IR spectrum of the synthesized Tl₂O₃ nanoparticles.

and adsorbed water molecules [11]. The resulting OH/ OL atomic ratio is much larger than previously reported values [12], confirming that the amount of adsorbed oxygen species is at a high level at the surface layer presumably due to the large surface-to-volume ratio of the nanoparticles. Dissolved oxygen can produce extra OH radicals and improve the degradation process.

Band gap energy of the loaded samples was estimated by the Kubelka-Munk function using Eq. (1).

$$\alpha = \frac{A(E_g - h\nu)^n}{h\nu} \tag{1}$$

where, E_g is the bandgap of the proposed semiconductor (eV), A is the constant, n is equal to 1/2 for direct transition, and α is the absorption coefficient defined by Beer-Lambert's law. A plot of transferred Kubelka-Munk versus the hv of Tl₂O₃ is shown in Fig. 6. From the graph, we can see that the bandgap value for Tl₂O₃ was 3.5 eV as compared with the band gap of bulk Tl₂O₃, which is 1.4 eV [13].



Fig. 5. XPS survey spectrum of the nanorod composite of Tl_2O_3 and O_{1s} spectra.



Fig. 6. Plot of transferred Kubelka-Munk versus energy of the light absorbed of the synthesized Tl_2O_3 nanoparticles.

3.2. Photodegradation of CPX

The photocatalytic process consists of absorption of a photon with an energy hv greater or equal to the bandgap energy E_g , which leads to the formation of an electron/hole pair in the semiconductor particle.

The degradation of CPX solutions at different times was monitored and analyzed by measuring the decrease in absorbance intensity at the maximum wavelength using a UV-Vis spectrophotometer. The effectiveness of the degradation was determined by the Eq. (2) [14,15].

$$\eta = \left[1 - \frac{C}{C_0}\right] \times 100 \tag{2}$$

where, C_0 and C are the concentrations of the initial (t = 0) and light exposed solutions for 't' minutes, respectively. Fig. 7 shows the reduction in the absorption spectra of CPX decomposition in the presence of Tl₂O₃ under UV light irradiation. Evidently, the absorption spectra decreased gradually with reaction time due to the degradation of CPX.

The effect of pH on the degradation extent of CPX was also studied (Fig. 8). The pH for the used Tl_2O_3 was obtained at about 8.47, based on the procedure reported in the literature [16]. The dissociation acidic constants for cephalexin are 2.6 and 6.9 [17,18]. In the pH range of 4-6, cephalosporins exhibited relatively slow degradation with optimum stability at pH=5 [19,20]. At strong basic pHs (pH = 9 in this work), the generated hydroxyl radicals can react with the hydroxyl anions present in the solution and produce other radicals with lesser activity, resulting in decreased degradation efficiency. Hence, attempts have been made to study the influence of pH in the degradation of CPX in the range of 5-9.



Fig. 7. Decrease in the UV-Vis absorption of CPX at its λ_{max} during the photo degradation process in a 50 folds diluted CPX solution, Tl₂O₃ 0.2 g.L⁻¹, and pH = 5.5.

To investigate the effect of Tl_2O_3 concentration on photocatalytic efficiency, a set of experiments were done at pH = 5.5 with different concentrations at a range of 0.1 - 0.3 g.L⁻¹. By increasing in the mass of the photocatalyst from 0.1 to 0.2 g.L⁻¹ the degradation activity first increased and there after decreased. Agglomeration increases at high dosages of the photocatalyst, thus the CPX degradation decreased because the production of the holes and hydroxyl holes are reduced (Fig. 9(a)).

The effect of initial CPX concentration on its degradation was investigated. The results show that the maximum photocatalytic elimination of CPX occurred at 50 times the diluted solution. At lower concentrations (100 times dilutions in this work),



Fig. 8. Effect of pH on the photodegradation extent of CPX at 50 folds dilution of the initial CPX solution, 0.2 g.L⁻¹ of the photocatalyst at pH = 5.5, 7, and 9.



Fig. 9. (a) Effect of dosage of the Tl_2O_3 photocatalyst on the photodegradation extent of CPX at 100 folds dilution of the initial CPX solution, pH = 5.5, and 0.1 g.L⁻¹ of the photocatalyst. (b) Effect of initial CPX concentration on its photodegradation extent at pH = 5.5.

the lifetime of hydroxyl radicals is low, reducing degradation efficiency. At further increases in CPX concentration (10 fold diluted solution), the available OH radicals are inadequate for the pollutant degradation, and the degradation rate of the pollutant decreases (Fig. 9(b)).

4. Conclusions

A simple co-precipitation method has facilitated the preparation of Tl₂O₃ in the presence of hexamine, which leads to the production of submicron x-shaped Tl₂O₃. The photocatalytic activity of Tl₂O₃ synthesized using hexamine has shown a supernatural degradation rate compared to previous studies. Various factors affect the degradation process, such as pH, initial CPX, and Tl₂O₃ concentrations, were analyzed and optimized. The CPX degradation was higher at pH 5.5, compared to pH values of 7 and 9. We found that 97% of CPX has been eliminated by the prepared Tl_2O_3 after 15 min. The observed decrease in the absorption intensity of the CPX solution confirms the degradation of CPX molecules to smaller fragments. The degradation of CPX molecules into smaller fragments can be attributed to the hydrolysis of the acetoxy ester grouping (as one photodegradation product) and cleavage of the

 β -lactam ring. The Tl₂O₃ played an important role in the photodegradation process. Heterogeneous catalysis proceeds via adsorption of reactant molecule(s) on the solid surface. Also, the generation of hydroxyl radicals is a function of pH.

Acknowledgment

We wish to thank the Islamic Azad university, Central Tehran branch, for its invaluable support throughout the project.

References

- M. Klavarioti, D. Mantzavinos, D. Kassinos, Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes, Environ. Int. 35 (2009) 402-417.
- [2] Q.P. Isariebel, J. Carine, Sonolysis of levodopa and paracetamol in aqueous solutions, Ultrason. Sonochem. 16 (2009) 610-615.
- [3] M.N. Amin, J.L. Zilles, J. Greiner, S. Charbonneau, L. Raskin, E. Morgenroth, Influence of the antibiotic erythromycin on anaerobic treatment of a pharmaceutical wastewater, Environ. Sci. Technol. 40 (2006) 3971-3977.
- [4] K. Choi, S.G. Kim, S.H. Kim, Removal of tetracycline and sulfonamide classes of antibiotic compound by powdered activated carbon, Environ. Technol. 29 (2008) 333-342.
- [5] G. Ciric-Marjanovic, Recent advances in polyaniline research: Polymerization mechanisms, structural aspects, properties and applications, Synthetic Met. 177 (2013) 1-47.
- [6] I.E. Wachs, G. Deo, M.A. Vuurman, H. Hu, D.S. Kim, J-M. Jehng, Molecular design of supported metal oxide catalysts: An initial step to theoretical models, J. Mol. Catal. 82 (1993) 443-455.
- [7] M.A. Vuurman, A. Oskam, D.J. Stufkens, I.E. Wachs, Structural determination of surface rhenium oxide on various oxide supports (Al₂O₃, ZrO₂, TiO₂ and SiO₂), J. Mol. Catal. 76 (1992) 263-285.
- [8] S. Avivi, Y. Mastai, A. Gedanken, A new fullerenelike inorganic compound fabricated by the sonolysis of an qqueous solution of TlCl₃, J. Am. Chem. Soc. 122 (2000) 4331-4334.
- [9] G.E. McGuire, G.K. Schweitzer, T.A. Carlson, Core electron binding energies in some Group IIIA, VB,

and VIB compounds, Inorg. Chem. 12 (1973) 2450-2453.

- [10] H.M. Kothari, A.A. Vertegel, E.W. Bohannan, J.A. Switzer, Epitaxial electrodeposition of Pb-Tl-O superlattices on single-crystal Au(100), Chem. Mater. 14 (2002) 2750-2756.
- [11] I.G. Casella, M. Gatta, Electrodeposition and characterization of nickel-copper alloy films as electrode material in alkaline media, J. Electrochem. Soc. 149 (2002) B465.
- [12] I.G. Casella, M.R. Guascito, M.G. Sannazzaro, Voltammetric and XPS investigations of nickel hydroxide electrochemically dispersed on gold surface electrodes, J. Electroanal. Chem. 462 (1999) 202-210.
- [13] E.D. Rosa, S. Sepúlveda-Guzman, B. Reeja-Jayan, A. Torres, P. Salas, N. Elizondo, M.J.J. Yacaman, Controlling the growth and luminescence properties of well-faceted ZnO nanorods, Phys. Chem. C, 111 (2007) 8489-8495.
- [14] R.J. Phillips, M.J. Shane, J.A. Switzer, Electrochemical and photoelectrochemical deposition of thallium (III) oxide thin films, J. Mater. Res. 4 (1989) 923-929.
- [15] L. Gnanasekaran, R. Hemamalini, K. Ravichandran, Synthesis and characterization of TiO₂ quantum dots for photocatalytic application, J. Saudi Chem. Soc. 19 (2015) 589-594.
- [16] L. Gnanasekaran, R. Hemamalini, R. Saravanan, K. Ravichandran, F. Gracia, V.K. Gupta, Intermediate state created by dopant ions (Mn, Co and Zr) into TiO₂ nanoparticles for degradation of dyes under visible light, J. Mol. Liq. 223 (2016) 652-659.
- [17] X. Yong, A.A. Martin Schoonen, The absolute energy positions of conduction and valence bands of selected semiconducting minerals, Am. Mineral. 85 (2000) 543-556.
- [18] E.H. Wiseman, E.C. Schreiber, R. Pinson Jr., The distribution, excretion and metabolism of benzquinamide, Biochem. Pharmacol. 13 (1964) 1421-1435.
- [19] W.H. Streng, Microionization constants of commercial cephalosporins, J. Phram. Sci. 67 (1978) 666-669.
- [20] M.E. Abdel-Hamid, FSQ spectrophotometric and HPLC analysis of some cephalosporins in the presence of their alkali-induced degradation products, I1 Farmaco, 53 (1998) 132-138.