POROUS SnO_2/TI DIMENSIONALLY STABLE ANODE FOR DEGRADATION OF POLLUTANTS FROM WATER: SYNTHESIS AND MORPHOSTRUCTURAL CHARACTERIZATION

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Abstract
In this work, the protocol based on *Doctor-Blade* method for synthesis of porous SnO_2/Ti dimensionally stable anode suitable for advanced treatment of water/wastewater is presented. Prior to SnO_2/Ti synthesis, SnO_2 was obtained by *sol-gel* method using $SnCl_2$ as Sn precusor and polyethylene glycol. The morpho-structural characterization through X-ray diffraction (XRD) and scanning electron microscopy coupled with energy-dispesive X-ray (SEM/EDX) confirmed an uniform deposition of SnO_2 mesoporous on the Ti surface with typical mud cracked-like structure, which should be suitable for the further water treatment application.

Introduction
Nowadays, the electrochemistry-based processes are tacking ground in the research field of advanced water/wastewater treatment technology. However, it is well-known that for the electrochemical process, besides their advantages, several drawbacks related to the energy consuming and the minimum conductivity required for water have been limited their practical application. To overcome these shortcomings, three-dimensional electrode materials are considered to develop the 3D electrochemical reactor [1]. The 3D electrochemical processes can be designed and customized function on the practical needs [2] and one of the main important element is the electrode material characterized by the specific features, e.g., electrocatalytic activity, high porosity, sorption capacity. Dimensionally stable anodes (DSA) are very well-known for advanced water treatment because of their high-catalytic activity towards pollutants destruction, relatively inexpensive and long life-time. Several types have been tested (e.g., TiO2, SnO2, RuO2, IrO2) in wastewater treatment and the most of them as thin films [3, 4]. Very good performances of the DSA-based electrochemical processes have been reported for the degradation of a large spectrum of organic pollutants from water but with high energy consuming or without their complete mineralization [5].
Three dimensional anodes based on specific configuration consisted of Ti filter electrodes array and activated carbon have been reported for efficient advanced wastewater treatment within 3D electrochemical reactor, considering high electroactive surface area combined with other electrochemical, mechanical and physical characteristics, which is direct linked to the characteristic morphological features [6].
In this work, the morpho-structural characteristics of porous SnO_2 on Ti substrate synthesized through *Doctor-Blade* method using SnO_2 paste prior synthesized from tin chloride precursors, envisaging its further usage in advanced treatment of water containing cystostatics as emerging

pollutants, are presented. The morpho-structural properties of the porous SnO_2/Ti are characterized by scanning electron microscopy coupled with energy-dispersive X-Ray (SEM/EDX) and X-Ray diffraction (XRD) methods.

Experimental

1.Pretreatment of titanium plates surface: First, a titanium plates (1 X 1 cm) was sanded with sandpaper P4000, followed by an ultrasonic treatment in distilled water for 30 min. Next, it was placed in a 10% (wt%) sodium hydroxide solution for 1 h at 80˚C and finally in a 10% (wt%) oxalic acid solution, for 2 h at 80˚C. Lastly, the Ti substrate were rinsed sequentially with acetone, ethanol and distilled water and the dried at 60˚C.

2. Preparation of SnO_2 mesoporous: Anhydrous tin chloride ($SnCl_2$, 99%, Aldrich) was used as a tin source, and polyethylene glycol Pluronic P-123 (Aldrich) was applied as the structure-directing agent. All of the chemicals were used without further purification. SnO_2 samples was synthesized using *sol-gel method* process as following: a solution was prepared by dispersing 1.5 g of Pluronic P-123 in 15 mL ethanol over 1 h at 40 °C. Then solution was mixed with 5 mL of $SnCl_2$, 10 mL distilled water under continuous stirring and then an appropriate amount of HCl was added to adjust the acidity of the solution. After 4 hours mixing the precipate was left standing to age for 48 h in Petri dishes at 40˚C. In order to obtain SnO_2 mesoporous the sample was treated in furnance in air atmosphere at 400˚C for 1 hour at a ramping rate of 1˚C/min.

3. Preparation of SnO_2 paste: SnO_2 solutions were prepared, according to following protocol: 0.3 g crystalline SnO_2 powder was mixed with a solution of ethyl cellulose and 2 ml α-terpinol and ultrasounded for 20 minutes. For a good homogenization, SnO_2 paste was placed in the ball mill (Lab Mills lx QM vertical planetary ball mill) at a frequency of 40 kHz for 12 hours. Finally, SnO_2 paste was deposited on Ti plates using a conventional one deposition of *Doctor-Blade* method. The SnO_2/Ti plate was then dried in air for 30 minutes, and a final annealing was performed at 300˚C for 1 hour at a ramping rate of 1˚C/min.

Results and discussion

In order to determine the crystal phase composition, X-ray diffraction measurements were carried out at room temperature using a PANalytical X'PertPRO MPD Difractometer with Cu tube in the region 2θ = 20–80º.

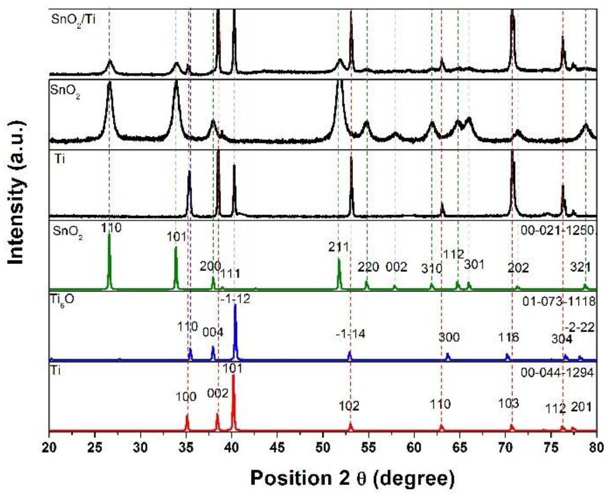
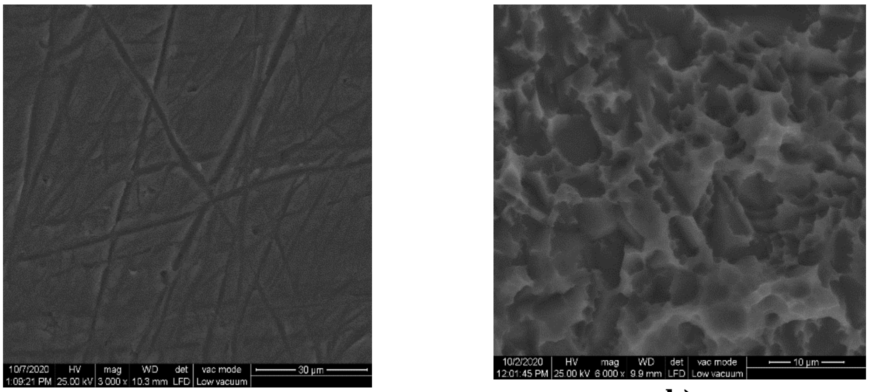


Fig. 1. XRD pattern for Ti plate, SnO_2 powder and SnO_2/Ti plate (electrode)

Figure 1 presents XRD patterns of the Ti plates, SnO_2 powder and SnO_2/Ti plates. The diffraction data at room temperature for SnO_2 compound ((110), (101), (200), (211), (220),

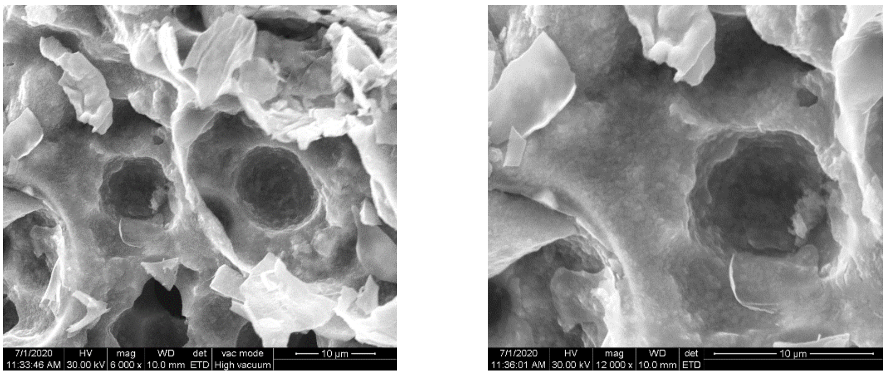
(002), (310), (112), (301), (321) - crystallographic planes, JCPDS card no.00-021-1250) indicates that the sample is well crystallized.
Also, XRD data evidence the presence of Ti peaks of the corroded Ti plates according to standard card JCPDS card no.00-044-1294((100), (002), (101), (102), (110), (103) (112)). The presence of Ti_6O according to standard card JCPDS card no.01-073-1118 (110) appear because of partial oxidation of Ti plate under acidic conditions.
These results show that the electrode composition prepared by *Doctor Blade* method can promote the uniform deposition of SnO_2 onto the Ti surface and SnO_2 mainly exists in its crystalline form.
The morphology of the Ti plates, SnO_2 powder and SnO_2/Ti electrode were examined comparatively through scanning electron microscopy (SEM) coupled with the energy dispersive X-Ray analysis detector (EDX).
From Figure 2 can be seen that the surface of Ti plates after corrosion treatment has a highly disordered, appears very rough and presents a cratered structure which should contribute to the good coating by the SnO_2 paste.



a) **b)**

Fig. 2. SEM images for Ti plates: a-untreated; b-pretreated (corrodated)

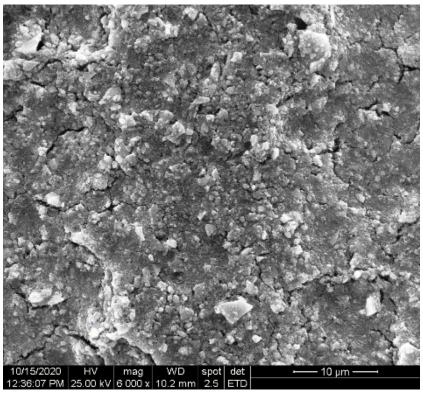
Figure 3 presents the SEM images for SiO_2 powder synthesized by sol-gel method and it can be highlight that the material has spongeous porous-mesoporous aspect with the almost equal dimensions. The formation of the chanels which give the spongeous aspect is due to the decomposition of the surfactant from the mesoporous systems during the thermal treatment.



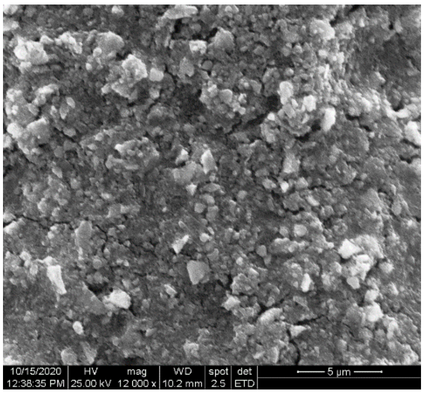
a) **b)**

Fig.3 SEM images for SnO_2 powder at different magnifications:
a)-6000x; b)-12000x

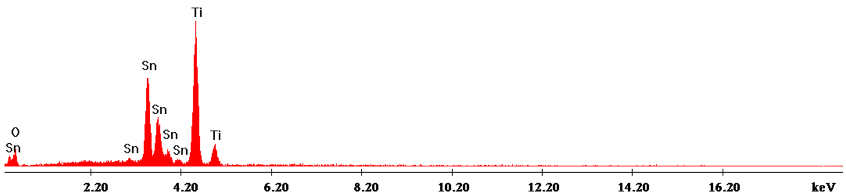
Figure 4 shows the SEM images and EDX spectrum of a SnO_2/Ti electrode prepared after one single layer deposition of *Doctor-Blade* method, which presents a typical mud cracked-like structure. The main reasons are the thermal treatment of the electrode coating and the cratered structure of titanium substrate. Afer the *Doctor-Blade* method deposition, the SnO_2/Ti maintained its highly porous structure which would facilitate the electroactive surface area increasing combined with a local preconcentration of the pollutant concentration onto the electrode surface, which should improve the overall oxidation/degradation process of the pollutants from water. The Ti and Sn content is evidenced also by EDX microprobe and it is in according with XRD results.



a)



b)



c)

Fig.4 SEM images for SnO_2/Ti electrode at different magnifications: a)-6000x; b)-12000x; c)-EDX image for SnO_2/Ti

Conclusions

The porous SnO_2/Ti dimensionally stable anode material was succesfully synthesized using the protocol based on *Doctor-Blade* method applied for the Ti plate prior corrodated under alkaline/acidic medium using SnO_2 paste. Also, SnO_2 was synthesized by *sol-gel* method using $SnCl_2$ as Sn precusor and polyethylene glycol. An uniform deposition of mesoporous SnO_2 on the Ti surface with typical mud cracked-like structure was found through X-ray diffraction (XRD) and scanning electron microscopy coupled with energy-dispesive X-ray (SEM/EDX). The morphostructural properties show that porous SnO_2/Ti dimensionally stable anode material exhibits great potential for further electrochemical studies envisaging the final water treatment application.

Acknowledgements

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References

1. C. Zhang, Y. Li, Z. Hu, L. Zhou, M. Zhou, Chem. Eng. J. 228 (2013) 455.
2. M. Uğurlus, S.I. Yilmaz, A.Vazoğullar, Materials Today: Proceedings 18 (2019) 1986.
3. L, Liang, H. Huanhuan, Z. Chao, W. Qian, Z. Minghua, Curr. Org. Chem.16 (2012) 2091.
4. S. Trasatti, Electrochim. Acta 45 (2000) 2377.
5. M. Ihos, C. Bogatu, I. Cristea, F. Manea, R. Pode, Rev. Chim. 67(8) (2016), 1462
6. Z. Liu, F. Wang, Y. L. Tianlong, X. S. Zhu, J. Env. Sci. 23(Supplement) (2011) S70.