Annals of the University of Craiova
The Chemistry Series
Volume L, No. 2 (2024) 26-29
homepage: chimie.ucv.ro/anale/

Efficient Ce-dopped mesoporous TiO_2 photoanode for simultaneous phenol degradation and electricity generation

Mihaela Mureseanu, Valentina Chivu, Cezar-Ionut Spinu, Nicoleta Cioatera*

University of Craiova, Faculty of Sciences, Department of Chemistry, Calea București 107 I, Craiova, Romania

* E-mail: mihaela_mure@yahoo.com

Received: 15.11.2024 / Accepted: 19.11.2024 / Published: 20.12.2024

Abstract:
New photoanodes for an efficient photocatalytic fuel cell (PFC) have been obtained by spin-coating the mesoporous Ce-doped TiO_2 thin film onto a bottom nanocrystalline TiO_2 layer prepared onto FTO conductive glass. All materials were characterized by XRD, SEM-EDX, UV-Vis, Raman, XPS spectroscopies and N_2 adsorption-desorption isotherms for their textural and structural characteristics and the chemical nature of their surface. The nanocomposite films were without cracks and consisted of small crystallite of anatase. The photocatalytic activity of the fabricated photoanodes was evaluated for phenol photodegradation in aqueous media under simulated solar light irradiation. Furthermore, the photoelectrochemical characterization evidenced the role of the titania compact layer, the effect of the TiO_2 mesoporous structure, the amount of cerium and the oxidation state of Ti and Ce in the new photocatalysts on the enhanced photovoltaic performance. Based on the obtained results these new photoanodes could be considered for the construction of an efficient PFC system.

Keywords: Ce-dopped mesoporous TiO_2, photocatalytic fuel cell, phenol degradation

1. INTRODUCTION

Photocatalytic Fuel Cells (PFCs) are one of the environmental-friendly technologies which consume an organic or inorganic fuel to produce renewable electricity and allow simultaneous treatment of different wastewater.

The photocatalyst in the form of mesoporous nanocrystaline titania (nc-TiO_2) semiconductor film was a good choice for a performant photoanode [1]. However, its applicability is hindered by low conversion efficiencies due to high electron-hole recombination rates and low visible light absorption. By TiO_2 doping with rare earth ions these limitations are overcoming. Cerium (Ce) is a favorable dopant due to the optical and catalytic properties that improved the photocatalytic activity, namely presence of the redox Ce^{3+}/Ce^{4+} couple, high thermal stability, high electrical conductivity and large oxygen storage capacity. For a Ce-doped TiO_2 thin film the better performances were correlated with the occurrence of Ce↔Ti intervalence charge transfer and associated oxygen vacancy formation [2].

In this work we have focused our efforts to prepare new photoanodes based on mesoporous TiO_2 films doped by direct synthesis with 2.5% and 5% CeO_2, with high surface area, thermally stable and enhanced photodegradation and photovoltaic activities.

2. MATERIALS AND METHODS

The synthesis of mesoporous TiO_2 (TGP) and TiO_2 modified with 2.5% and 5% CeO_2 (TGP2.5C and TGP5C) was carried out by sol-gel process in presence of Pluronic block copolymer surfactant and evaporation-induces self-assembled (EISA) method [3]. For the phoanodes preparation, in the first step, a bottom layer of TiO_2 synthesized by the sol-gel method was deposited onto FTO glass (TF). The mesoporous TiO_2 or Ce-modified TiO_2 were deposited on the top of the calcined nanocrystalline TiO_2 layer using the gels aged in Petri dishes for 2h at 35-40^{0}C by spin-coating method. After mesoporous layer deposition, the films were dried at 80^{0}C for 4h and annealed at 400^{0}C for 4h (TGP_TF, TGP2.5C_TF and TGP5C_TF). The obtained nanomaterials were characterized by conventional techniques, including XRD, SEM-EDX, N_2 adsorption-desorption, XPS, UV–Vis and Raman spectroscopies. The photo electrochemical analysis was performed in a three-electrode photo electrochemical cell. The cell in a two-electrode configuration was employed in the measurements of the PFC performance parameters. The photocatalytic activity was measured based on the degradation of an aqueous phenol solution with a concentration of 1.0 g L^{-1} under simulated solar light irradiation.

3. RESULTS AND DISCUSSION

The Ce-modified TiO_2 layer has a compact and uniform glasslike surface morphology with some minor crack defects. The nanocrystaline titania film was quite compact and homogeneously constituted of primary particles sized about 100 nm. For the mesoporous titania and cerium doped titania the film became more compact with smaller particles. The EDX spectra confirms the existence of Ce, Ti, and O elements and this observation is consistent with the cerium amount considered for synthesis. The X-ray diffraction patterns of the Ce modified TiO_2 film consisted only of anatase and none Ce-containing phases were observed. The major (101) anatase peak intensity decreased after Ce introduction. All the prepared films were transparent with a pale-yellow color in the case of Ce-modified TiO_2. For Ce-doped TiO_2 films the absorption threshold wavelength shifts to the red (narrow bandwidth). The impact of Ce-doping on the photo electrochemical properties was discussed, including the photocurrent response, flat-band potential, Fermi level, charge carrier density (N_d), space-charge layer width (W) and charge transfer behavior (Electrochemical impedance spectroscopy-EIS) and correlated with the current-voltage characteristics of the PFC constructed with the new photo anode. The electrical performances of the photo-combustion cell constructed with these photoanodes are presented in Table 1. The J_{SC} and JV_{max} values are comparable with the data in the literature for the same type of materials [4]. Interestingly, the best results were obtained for non-doped mesoporous TiO_2. For samples doped with Ce, the Ce^{3+} ions probably act as an electron trap, and the current density in the external circuit is lower. However, this property has been shown to be beneficial for phenol degradation under visible light irradiation. In the phenol photo degradation tests, better results were obtained for the thin film anode (TGP5C_TF) in comparison with the powder photo catalysts, due to a better exposure of the active centers to the UV-Vis light irradiation and a greater contact surface area with the aqueous media.

Table 1. The current-voltage characteristics of the presented PFC*

Anode	J_{SC} (μA/cm²)	V_{OC}	JV_{max} (mW/cm²)
TF	304.81	0.97	319.05
TGP_TF	274.13	0.96	266.99
TGP2.5C_TF	84.78	0.96	287.87
TGP5C_TF	71.64	0.96	395.02

* Fuel: 0.2M Na_2SO_4 +0.2M CH_3COOH (pH 4.6)

4. CONCLUSION

New photoactive Ce-doped TiO_2 mesoporous thin films have been successfully prepared on FTO substrate by a sol-gel method. The textural and structural characterization of these materials supported their high crystallinity and mesoporous structure. The presence of the TiO_2 anatase crystalline phase and the high surface area were proved to be beneficial both to generate photoelectrons and to adequately transfer the electrons to an external circuit with undergoing a less electron loss at the electrode/electrolyte interface. Furthermore, by cerium introduction as CeO_2 on the surface of the mesoporous TiO_2 the phenol degradation efficiency was enhanced under simulated solar light irradiation (best results for TGP5C_TF samples). Based on the obtained results, this new photoanodes could be considered for the construction of an efficient photo electrochemical system.

REFERENCES

[1] W. Guo, T. Guo, Y. Zhang, L. Yin, Y. Dai, *Chemosphere*, 339 **(2023)**139486.
[2] L. Chung, W.-F. Chen, P. Koshy, C. C. Sorrell, *Mater. Chem. Phys*. 197 **(2017)** 236.
[3] M. Mureseanu, V. Chivu, M. Osiac, M. Ciobanu, C. Bucur, V. Parvulescu, N. Cioatera, 2021, *Catal. Today* 366 **(2021)** 164.
[4] S. Roy, J. Darabdhara, M. Admaruzzaman, *Environ. Res*. 236 **(2023)** 116702.