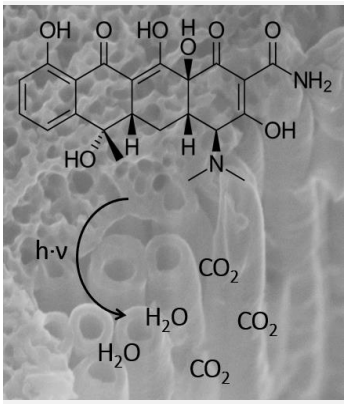
Potential Application of Anodized HfNbTaTiZr High Entropy Alloy as Photocatalyst

ORAL/POSTER
Ph.D. Student: Y/N
Journal: JECE

B. Ljubec Božiček[1,2], *L. Einfalt*[1,2], *M. Čeh*[1], *B. Alcantara Marinho*[1]. *(1) Jožef Stefan Institute, Jamova 39, Ljubljana, Slovenia, barbara.ljubec.bozicek@ijs.si. (2) Jožef Stefan International Postgraduate School, Jamova 39, Ljubljana, Slovenia.*



The heterogeneous photocatalysis process is a green technology for the degradation of organic pollutants in water that present low removal efficiency by conventional treatment processes. A lot of effort is being put into developing new and highly active photocatalysts to address this issue. Lately, high entropy alloys (HEA) have gained unprecedented attention in the field of heterogeneous photocatalysis since there exist numerous opportunities to conceive new HEA-based photocatalysts with improved photocatalytic activities. Therefore, in this study, a highly ordered nanotubular mixed metal oxides layer, firmly attached to the HfNbTaTiZr HEA support has been successfully synthesized with the facile anodic and thermal oxidation process. The prepared mixed metal oxide photocatalysts exhibited lower band gap values compared to individual oxides. Moreover, the synthesized photocatalyst exhibited enhanced catalytic efficiency and kinetics in the degradation of tetracycline in water.

Introduction

Photocatalytic oxidation techniques are promising and highly efficient processes for the degradation of antibiotics from wastewater into nontoxic products of CO_2 and H_2O. These processes produce highly active radicals at ambient temperature and pressure. Furthermore, they are classified as green processes since the required radiation energy can be provided by renewable sources [1]. There are many reports on the photocatalytic degradation of antibiotics using diverse photocatalysts, such as titanium dioxide, zinc oxide, tungsten trioxide, metal organic frameworks, and carbon quantum dots [2]. However, the photocatalytic activity of most of these photocatalysts is restricted by insufficient absorption of visible to near-infrared light, rapid recombination of charge carriers, and lack of adequate catalytically active sites. Currently, high-entropy alloys (HEA) are attracting great attention for catalytic applications due to their outstanding chemical in physical properties originating from high entropy configuration of five or more elements in equal atomic compositions. Therefore, HEAs could provide a new platform for screening efficient photocatalysts offering more opportunities to tune the catalytic properties than conventional photocatalysts. However, the synthesis methods for HEA-based photocatalysts can be very complex, requiring multiple steps and extreme conditions [3]. Furthermore, there are rare studies with a comprehensive understanding of the catalytic potential of HEAs for their practical applications. In line with all mentioned, herein a HfNbTaTiZr HEA was oxidized with a facile anodization and annealing method to form a nanotubular mixed metal oxide layer to be used as an efficient photocatalyst for degradation of the antibiotic tetracycline (TC).

Material and Methods

Anodization and annealing of HfNbTaTiZr HEA: The pristine HfNbTaTiZr HEA discs with dimensions l x Φ = 1 x 20 mm were purchased from China Leadmat Advanced Material Ltd. The supplier produced the mentioned discs via vacuum melting technique. The discs were firstly anodized in a two-electrode system [4] at constant potentials of 10–60 V for 2 h in an electrolyte 75 vol. % glycerol (≥ 99 %, Fisher Scientific) + 25 vol. % deionized H_2O + 0.25 M NH_4F (≥ 99.99 %, Sigma Aldrich). The anodized HfNbTaTiZr HEA had a rectangular area of around 10 mm^2. After anodization, discs were annealed in a muffle furnace (Nabertherm) at temperatures of 250–1000 °C for 1 h in air atmospher.

Chemical and physical characterization: The synthesized nanotubular oxide layers on HfNbTaTiZr HEA discs after anodization and annealing were characterized by scanning electron microscopy (Verios 4G HP, Thermo Fisher) to investigate the morphology and chemical composition, Raman spectroscopy (NTEGRA Spectra Confocal Raman) to determine the crystallinity, and diffuse reflectance with UV-Vis spectrophotometry (Lambda 950, PerkinElmer) for the estimation of the band gap.

Photocatalytic degradation of model compound: The prepared nanotubular oxide layers on HfNbTaTiZr HEA were tested for photocatalytic degradation of the tetracycline (TC) with an initial conc. of 10 mg/L (≥ 99.0 %, Sigma-Aldrich) in a custom-made photoelectroreactor (APRIA Systems) with a quartz window and titanium as counter electrode. The TC solution was illuminated with a UV light of 365 nm and flux of 10 mJ/cm^2 and recirculated through the reactor at 1500 mL/min. Samples were periodically collected up to 60 min and analyzed with UPLC-PDA at 357 nm (Waters ACQUITY I-Class).

Results and Discussion

Pristine HfNbTaTiZr HEA consisted of a few 100 µm large grains with body-centered cubic crystal structures and contained a uniform distribution of all five elements. The pristine HfNbTaTiZr HEA was electrochemically anodized and the resulting outcome was the formation of a self-ordered mixed metal oxide nanotubes layer. The outer diameter of the nanotubes increased from 25 ± 1.2 nm to 140 ± 1.3 nm with increasing voltage from 10 V to 60 V. whereas the length of the nanotubes was around 10 µm and did not show voltage dependency. The presence of a random and dispersed unordered layer called nanosponge was also noted on the top region of the nanotubes. The oxide nanotube layers prepared at 10 V were further annealed under different temperatures. The morphological structure of nanotubes stayed untacked at temperatures 250, 350, 450, and 550 °C, while the one annealed at 1000 °C sintered and collapsed (Figure 1). The Raman analysis of the nanotube oxide layer of the samples anodized and annealed up to 550 °C showed an amorphous structure, whereas the sample annealed at 1000 °C showed a crystalline Raman spectrum similar to the literature reported $TiZrNbHfTaO_{11}$ [5]. In addition, the band gap value of the sample annealed at 1000 °C was considerably low 2.8 eV, when compared to the other samples (3.2 to 3.9 eV) or TiO_2 (3.2 eV). In the last part of our study, the prepared oxide nanotube layers were tested for photocatalytic degradation of antibiotic TC. The reaction degradation efficiency and its kinetic constant were the lowest for the only anodized oxide layer (Table 1). On the contrary, higher and nearly similar photocatalytic degradation results were achieved with annealed oxide layers, except for the one annealed at 250 °C, which surprisingly showed the highest degradation and kinetics despite the similar band gap value. Apparently, the band gap value and crystallinity of the photocatalysts showed no noticeable impact on the degradation reactions. Therefore, additional characterization must be performed to fully understand this new class of materials.

Table 1. List of properties of nanotube oxide layers and reaction

Voltage	Nanotube diameter	Annealing temperature	Band gap	Degradation of TC (C/C_0)	Kinetic constant ($k \times 10^{-3}$)
10 V	25 ± 1.2 nm	/	3.8 eV	0.75	4.3 ± 0.4 min^{-1}
20 V	40 ± 0.9 nm	250 °C	3.9 eV	0.40	11.1 ± 1.5 min^{-1}
30 V	55 ± 0.8 nm	350 °C	3.6 eV	0.58	7.2 ± 0.3 min^{-1}
40 V	78 ± 1.0 nm	450 °C	3.2 eV	0.66	7.1 ± 0.5 min^{-1}
50 V	125 ± 0.9 nm	550 °C	3.7 eV	0.57	6.3 ± 0.5 min^{-1}
60 V	140 ± 1.3 nm	1000 °C	2.8 eV	0.65	6.6 ± 0.4 min^{-1}

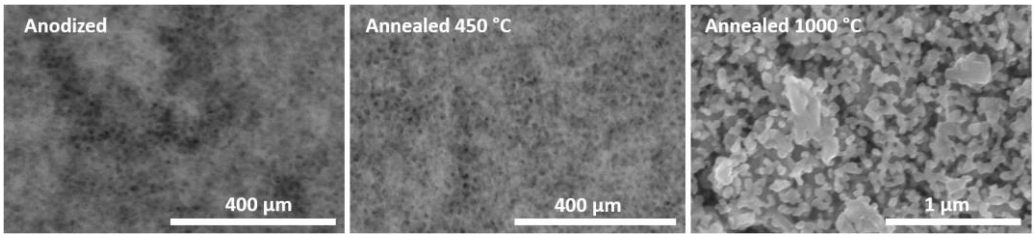


Figure 1. The SEM top-down images of anodized and annealed nanotube oxide layers on HfNbTaTiZr HEA.

Conclusions

With this study, it has been proven that anodization and annealing methods are effective synthesis approaches for growing self-ordered mixed metal oxide nanotube layers on HfNbTaTiZr HEA. As well as, synthesized nanotube oxide layers can be considered as promising photocatalysts for removal of antibiotics from water.

Acknowledgments

The authors gratefully acknowledge the Slovenian Research Agency (ARIS) for financial support within the project P2-0084. This work has also received funding from the European Union's Horizon research and innovation programme under the HORIZON-WIDERA-2022-TALENTS-02 grant agreement No. 101090289.

References

[1] B. Alcantara Marinho, L. Suhadolnik, B. Likozar, et al., *Journal of Cleaner Production*, 343 (2022) 131061.
[2] S. Das, M. Sanjay, A. R. S. Gautam, et al., *Journal of Environmental Management*, 342 (2023) 118081.
[3] S. Aydinyan, H. Kirakosyan, A. Sargsyan, et al., *Ceramics International*, 48 (2022) 20294.
[4] Ž. Marinko, L. Suhadolnik, Z. Samardžija, et al., *Catalysts*, 10 (2020) 803.
[5] S. Akrami, Y. Murakami, M. Watanabe, et al., *Applied Catalysis B: Environment and Energy*, 303 (2022) 120896.