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TiO_2@G-M (M:Ni,NiBi) Catalyst Production, Characterization and Application for Hydrogen Evolution Reaction

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In this study, nano scale electrocatalyst production, characterization and application for hydrogen evolution reaction was aimed. For this purpose, TiO_2 nanotubes were achieved by anodizing on Ti substrate then graphite intercalated on anodized surface and finally nickel and bismuth nano particles were electrochemically deposited on this surface. Produced electrodes were symbolized as TiO_2@G-M (M:Ni,NiBi). The electrocatalytic performance of these electrodes were investigated in 1 M KOH for hydrogen evolution reaction (HER). The characterization was achieved by cyclic voltammetry, scanning electron microscopy and energy dispersive X-ray analysis. The water wettability characteristics of electrode surfaces were investigated using contact angle by optical tensiometer. The Young-Laplace equation was used for calculations. The electrochemical behaviour was determined via linear sweep voltammetry, electrochemical impedance spectroscopy and polarization curves. Results showed that, nano-structured Ni and Bi deposited-graphite intercalated-titanium oxide nano-tubes (TiO_2@G-NiBi) decrease the hydrogen over potential and increase HER efficiency in alkaline solution.

Keywords: Nanotubes, Anodizing, Hydrogen Evolution Reaction (HER)

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1. Introduction

Energy demands, rising population and environmental pollution give direction to academic studies on renewable and sustainable energy. Today, in place of fossil fuels hydrogen is considered ideal-storable-environmentally friendly-alternative energy source [1]. There are many hydrogen production methods but, water electrolysis has crucial importance [2]. Because this method generates high purity hydrogen gas and it is technologically simple [3,4]. The main restricting factor of method is over-potentials in electrolysis cell. In order to minimize over potentials especially catalytic active materials have been design as cathode and anode materials [5-8]. These materials should be significantly effective, abundant, cheap and environmentally friendly. TiO_2 have been extensively studied for this purpose. In photo-electrochemical water splitting it has many advantages because of its chemical stability, non-toxicity and available price [9]. Researchers can shape TiO_2 as nano-rods, nano-tubes and nano-particles which enables the larger surface area and enhances catalytic activity. Anodizing is convenient procedure to achieve nano-tubes on Ti substrate. The tube diameters, legends wall thickness are adjustable via anodizing operation parameters which are applied potential-current, operation time, electrolyte type, etc [10,11]. Furthermore, electrode activity can be improved with the help of metal decoration on nano-tubes' mouth. In our previous study, extrinsic and intrinsic properties of Ti cathode is improved with the two steps procedure. The titanium oxide nano-tubes were produced then immediately it was doped nano-structured Ni and Mo particles [6]. The comparison of charge transfer resistance (Rct) at -1.5 V revealed that modified electrode decreased Rct almost $2.3x10^3$ times and increased hydrogen evolution reaction efficiency, significantly. Baran et al. [12] doped TiO_2 nano-tubes with Ag and DLC. After 1h electrolysis obtained Tafel slopes were 217.3 and 96.2 mV dec^{-1} and Rct values at -1.4 V were 43.97 and 16.81 ohm cm^2 for TiO_2 and TiO_2-NT-Ag/DLC, respectively. Guayaquil-Sosa et al. [13], produced meso-TiO_2 and doped with Pt in order to determine photocatalytic hydrogen production performance. The maximum Quantum yields for 2.50 wt% Pt/Meso was 22.6% in the same condition for commercial Degussa P25 TiO_2, value was 3.5%.

In this work, we have synthesized TiO2 nanotubes on Ti substrate then graphite was intercalated on surface and Ni,Bi decoration was achieved via galvanostatic method. The produced electrode was used as cathode in alkaline electrolysis cell.

2. Experimental details

The 99.9% pure Ti was used in this study and titanium oxide nano-tubes were produced on Ti surface with the help of anodizing procedure [6]. Anodizing procedure was achieved in 0.1 M HF and DC supply was MPS-3003L-3 instrument, Pt sheet with 2cm2 surface area was used as counter electrode, operation temperature was 298K. The 17.5 V anodizing potential applied during 30 min. The realization of extremely thin graphite layer was achieved simply by polishing a graphite rod on anodized surface (TiO_2@G) The electrodeposition of Ni and Bi were performed by using Iviumstat Electrochemical Interface. The Ag/AgCl (3 M KCl) electrode was used as the reference electrode. The nickel deposition bath composition was 30% $NiSO_4.7H_2O$, 1% $NiCl_2.6H_2O$, 1.25% H_3BO_3. The bismuth deposition bath composition was 0.1 M $Bi(NO_3)_3.5H_2O$ and 0.1 M tartaric acid ($C_4H_6O_6$) containing 1 M HNO_3. The molar ratio of Ni/Bi in the bath was 99.5:0.5 The constant current density of 5 mA cm^{-2} was applied and 100 µg metal was deposited per cm^{-2} of electrode surface, operation time was calculated via Faraday's laws. The other electrochemical measurements were carried by using CHI 660D A.C. electrochemical analyzer at room temperature, open to atmosphere in 1 M KOH. The cyclic voltammetry measurements were obtained in the potential ranges between −2.0 V and 0.8 V (vs. Ag/AgCl) with a scan rate of 0.1 V s^{-1}. The polarization curves were obtained with a scan rate of 0.001 Vs^{-1}. The EIS results were presented using a Zview software. The photoelectrocatalytic activity was determined under 100 mW cm-2 simulated AM 1.5 G solar light irradiation (Abet Solar Simulator Sun 2000). The surface characteristics of electrodes were examined by SEM. The SEM images were taken using a Carl Zeiss Evo 40 SEM instrument at high vacuum and 10 kV EHT. The chemical composition of the electrodes surface was investigated by energy dispersive X-ray spectrometer (EDX), a part of SEM device. The contact angles of bi-distilled water on electrode surfaces were determined by Biolin Scientific Attension Theta Lite Optical Tensiometer.

3. Results and discussion:

The cyclic voltammograms of all electrodes were given in Fig. 1. The peak at −0.71 V, corresponds to Ni/Ni^{2+} and V/V^{2+} oxidation, the transformation of α-$Ni(OH)_2$ to β-$Ni(OH)_2$ takes place between the potential ranges of −0.59 – 0.35 V. Then Ni^{2+}/Ni^{3+} transition is seen. Bi/Bi^{3+} oxidation is seen almost -0.4 V [14].

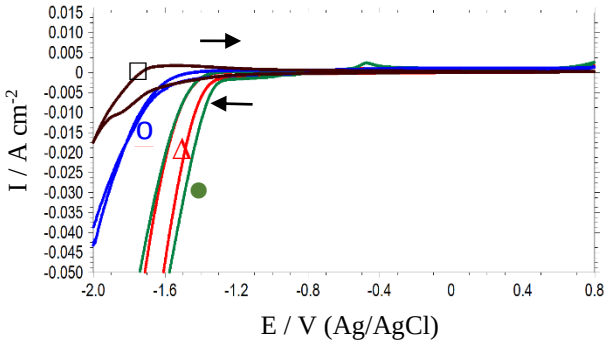

Fig.1: The cyclic voltammograms of TiO_2 (□), TiO_2@G (o),TiO_2@G-Ni (Δ), TiO_2@G-NiBi (•) in 1 M KOH solution, scan rate 0.1 V s^{-1}.

In Fig. 1 the highest HER activity was seen for TiO_2@G-NiBi, the onset of HER was seen at -1.49; -1.34 and -1.32 V (vs. Ag/AgCl) for TiO_2@G; TiO_2@G-Ni and TiO_2@G-NiBi, respectively.

The SEM image and EDX result of TiO_2@G-NiBi were given in Fig.2. Homogeneous and rough surface was seen for electrode and EDX result proved that C, N, and Bi were detected.

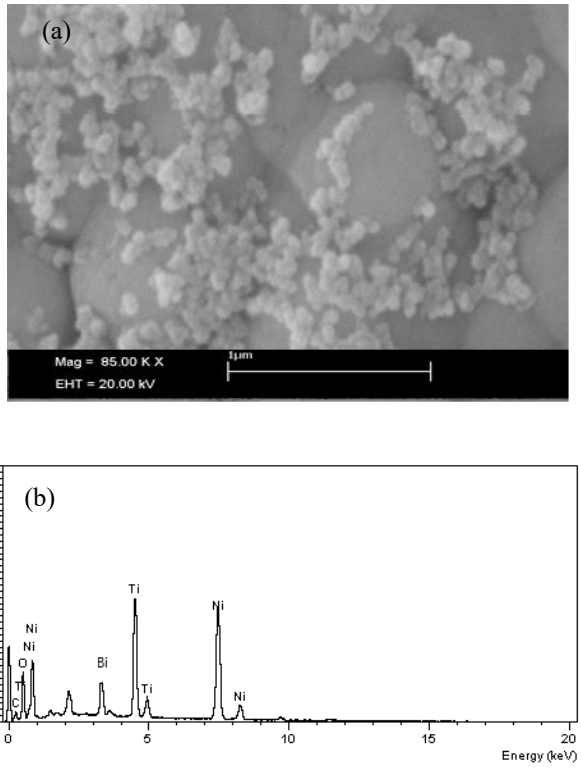

Fig.2: SEM image (a) and EDX (b) of TiO_2@G-NiBi

The cathodic polarization curves were presented in Fig.3.

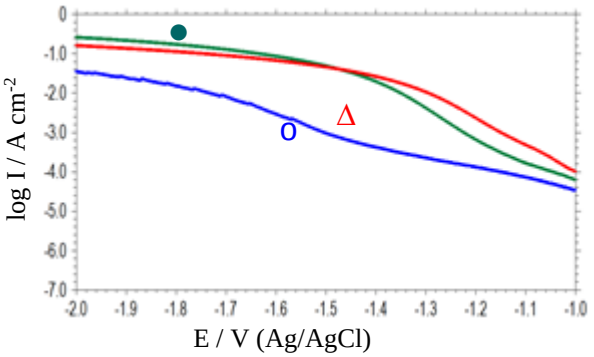

Fig.3: Figure 3. The cathodic polarization curves of TiO_2@G (o),TiO_2@G-Ni (Δ), TiO_2@G-NiBi (•) in 1 M KOH solution.

In Fig. 3, the highest HER activity is detected for TiO_2@G-NiBi. The -βc values were 342.4 mV/dec; 145.9 and 129.1 mV/dec for TiO_2@G (o),TiO_2@G-Ni (Δ) and TiO_2@G-NiBi (•), respectively.

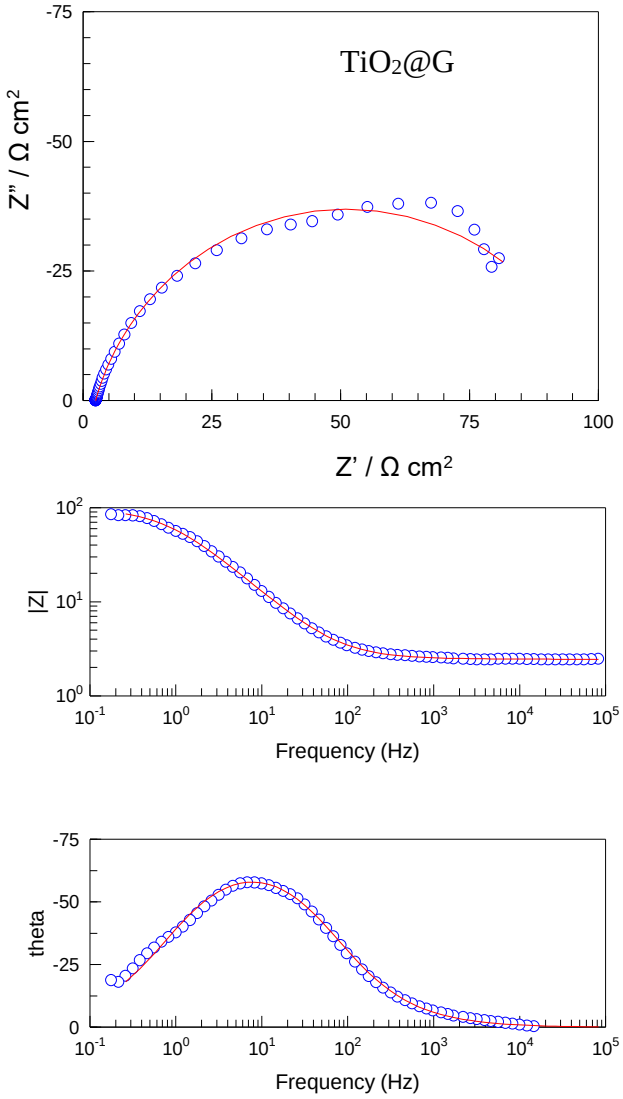

Fig.4: The Nyquist and Bode plots of TiO_2@G (o) and fit results (-), in 1 M KOH solution at -1.5 V (vs. Ag/AgCl).

In Fig. 4, solution resistance; Rs was 2.5 and polarization resistance; Rp was 97.28 ohm cm^2, respectively. CPE was $2.645x10^{-3}$/ s^n Ω^{-1} cm^{-2}. The Rp decreased dramatically after Ni decorated electrode surface and obtained results were presented in Fig. 5. It is known that lower resistance value is associated with higher activity.

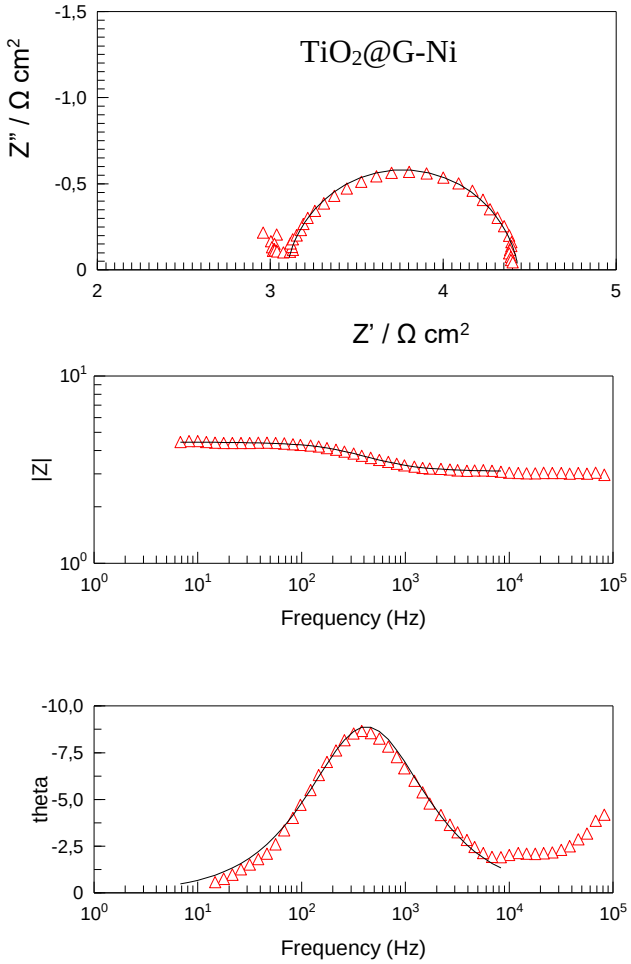

Fig.5: The Nyquist and Bode plots of TiO_2@G-Ni (Δ) and fit results (-), in 1 M KOH solution at -1.5 V (vs. Ag/AgCl).

In Fig. 5 obtained Rs and Rp were 3.1 and 1.34 ohm cm^2, respectively. The CPE was $0.689x10^{-3}$/ s^n Ω^{-1} cm^{-2}. According to literature Rp of TiO_2@G-Ni was favoroable for HER but we try to decrease Rp with the help of co-deposition of Ni and Bi. The Nyquist and Bode plots of TiO_2@G-NiBi were given in Fig.6. The lowest Rp was detected for TiO_2@G-NiBi, which was 1.05 ohm cm^2. The CPE was $1.73x10^{-3}$/ s^n Ω^{-1} cm^{-2}. The EIS parameters were presented in Table 1, according to fitting model which was given in Fig. 7.

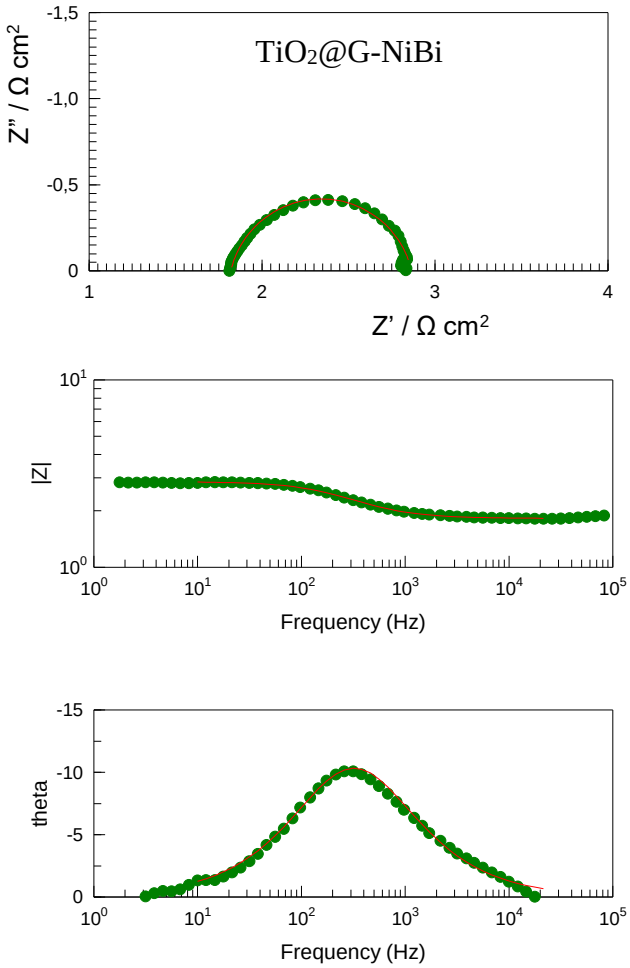

Fig.6: The Nyquist and Bode plots of TiO_2@G-NiBi (•) and fit results (-), in 1 M KOH solution at -1.5 V (vs. Ag/AgCl).

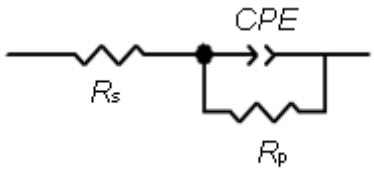

Fig.7: The equivalent circuit diagram

Table 1: EIS parameters of the catalysts at -1.5 V.

Electrode	*Rp (ohm cm²)*	*CPEx10⁻³* ($s^n\ \Omega^{-1}$ cm^{-2})	*n*	*θ (degree)*
TiO_2@G	97.28	2.65	0.83	57.72
TiO_2@G-Ni	1.34	0.69	0.91	8.66
TiO_2@G-NiBi	1.05	1.73	0.86	10.06

According to EIS results TiO_2@G-NiBi was convenient for HER. In order to better comparison EIS measurements were continued for different cathodic potentilas and results were given in Fig. 8.

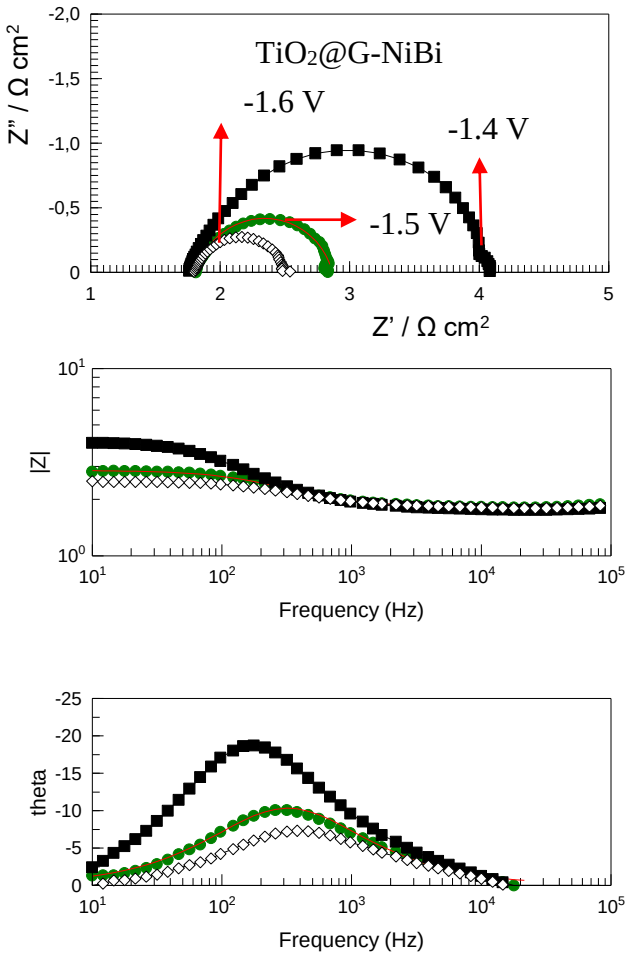

Fig.8: The Nyquist and Bode plots of TiO_2@G-NiBi in 1 M KOH solution at -1.4 V (■); -1.5 V (•); -1.6 V (◊) (vs. Ag/AgCl).

Table 2: EIS parameters for TiO_2@G-NiBi at different potentials.

E (V vs. Ag/AgCl)	*Rp (ohm cm²)*	*CPEx10⁻³* ($s^n\ \Omega^{-1}$ cm^{-2})	*n*	*θ (degree)*
-1.4	2.32	1.42	0.87	18.72
-1.5	1.05	1.73	0.86	10.06
-1.6	0.69	1.95	0.85	7.32

As seen from Table 2, Rp was decreased with increasing cathodic potential. The comparison of values with literature signaled that TiO_2@G-NiBi has application potential in electrolysis systems as a cathode material.

Kaninski et al. [15] used Co-W activated Ni electrodes for the hydrogen production from alkaline water electrolysis. The Rct value was 135.3 ohm cm^2 at 250 mV over potential. Another study about Ni–W catalyst was clarified that double layer capacitance (Cdl) was 0.01 F cm^{-2} and Rct was 0.868 ohm cm^2 at 300 mV (vs Hg/HgO) over potential [16]. The $Ni(OH)_2/MoS_2$ exhibited almost 1.5 ohm Rct at 200 mV over potential (vs RHE) and Cdl was 735 mF cm^{-2} [17].

Furthermore the electrochemical performance of TiO_2@G-NiBi was investigated under 100 mW cm^{-2} simulated solar light irradiation and results were given in Fig. 9.

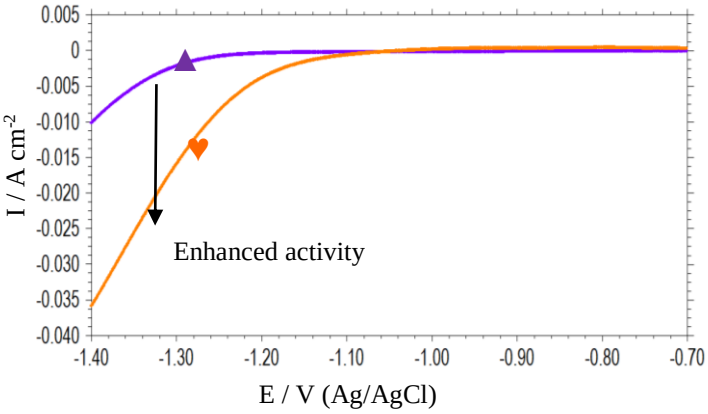

Fig.9: The linear sweep voltammogram under dark (▲) and light (♥) of TiO_2@G-NiBi..

As seen from Fig. 9 the cathodic current density increased under simulated solar light and the onset of cathodic reaction which was illustrated with HER was seen at lower potential.

Conclusion

In this study highly effective TiO_2@G-NiBi cathode was produced as a HER catalyst in alkaline electrolysis procedure. TiO_2@G-NiBi was fabricated with electrochemical methods on Ti substrate. TiO_2@G-NiBi decreased polarization resistance almost 89.8 times at -1.5 V (vs Ag/AgCl) and enhanced HER activity. Under 100 mW cm^{-2} simulated solar light irradiation cathodic onset potential was -1.1 V (vs Ag/AgCl). Consequently TiO_2@G-NiBi was offered as cathode in alkaline electrolysis cell.

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References:

[1] N.Mahmood, Y.Yao, J. Zhang, L. Pan, X. Zhang, J. Zou, Adv. Sci., 5 (2018) 1700464-1700487.
[2] F. Ganci, S. Lombardo, C. Sunseri, R. Inguanta, Renewable Energy, 123 (2018) 117-124.
[3] J. He, A. Chen, M. Chang, L. Ma, C. Li, J. Ind. Eng. Chem., 19 (2013) 1112–1116.
[4] H. He, A. Chen, H.Lv, H. Dong, M. Chang, C. Li, Appl. Surf. Sci., 266 (2013) 126– 131.
[5] A. Gomez Vidales, K. Choi, S. Omanovic, J. Int. Hydrogen Energy, 43 (2018) 12917-12928.
[6] M.E. Mert, B. Doğu Mert, G. Kardaş, B. Yazıcı, Appl. Surf. Sci., 423 (2017) 704-715.
[7] S. Shiva Kumar, S.U.B. Ramakrishna, S. Vijaya Krishna K. Srilatha, B. Rama Devi, V. Himabindu, South African Journal of Chemical Engineering 25 (2018) 54
[8] R. Wang, L. Guo, H. Jin, L. Lu, L. Yi, D. Zhang, J. Chen, Int. J Hydrogen Energy, 43 (2018) 13879-13886.
[9] L. Ma, A. Chen, Z. Zhang, J. Lu, H. He, C. Li, Catalysis Commun. 21 (2012) 27–31.
[10] K. Chung, S. Jeong, B. Kim, J.Kim, Y. Park Sang-Chul Jung, Int. J Hydrogen Energy, 43 (2018) 5873-5880.
[11] N. B. Kondrikov, P. L. Titov, S. A. Schegoleva, M. A. Khorin, Physics Procedia 86 (2017) 37 – 43.
[12] E. Baran, Z. Baz, R. Esen, B. Yazici Devrim, Appl. Surf. Sci. 420 (2017) 416–428.
[13] J.F. Guayaquil-Sosa, B. Serrano-Rosales, P.J. Valades-Pelayo, H. Lasa, Applied Catalysis B: Environmental 211 (2017) 337–348.
[14] M.E. Mert, G. Kardaş, J. Alloys Compd. 509 (2011): 9190-9194.
[15] M.P.M.Kaninski, S.M. Miulovic, G.S. Tasic, A.D. Maksic, V. M. Nikolic, Int. J Hydrogen Energy, 36 (2011) 5227-5235.
[16] M.P.M. Kaninski, D.P. Saponjic, I.M. Perovic, A.D. Maksic, V.M. Nikolic, Applied Catalysis A: General 405 (2011) 29– 35.
[17] B. Zhang, J. Liu, J. Wang, Y. Ruan, X. Ji , K. Xu, C. Chen, H. Wan, L. Miao, J. Jiang, Nano Energy 37 (2017) 74–80.