

Nanoparticles supported on Bi₂O₃ for direct formic acid fuel cells

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HIGHLIGHTS

- > Pt nanoparticles obtained over Bi₂O₃ by microwave heating.
- > Formic acid oxidation reaction with this catalyst was investigated.
- > The Pt/Bi₂O₃ showed good catalytic activity and stability.
- > Pt/Bi₂O₃ catalyst is a potential anode electrode material for the electro-oxidation of formic acid.

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ABSTRACT

Direct formic acid fuel cells (DFAFCs) are one of the potential power sources for the rapidly growing requirement of portable devices. Carbon has traditionally been the most common material of choice for DFAFCs electrocatalyst supports. In this study, Bi₂O₃ was used for support material because of some advantages, such as high corrosion resistance and durability. Bi₂O₃ supported Pt catalyst was prepared by using microwave irradiation technique. The catalyst was characterized by using SEM/EDS, XRD and FTIR analyzes. Electrocatalytic activity of Pt/Bi₂O₃ catalyst for formic acid oxidation was tested with cyclic voltammetry (CV) and chronoamperometry measurements.

1. Introduction

In recent years, formic acid has been used as an important fuel either without reformation (in direct formic acid fuel cells). Platinum (Pt) is the most common catalyst in both anode and cathode fuel cell reactions. When formic acid is used as fuel, the oxidation of formic acid on Pt catalysts often occurs via a dual pathway mechanism, which hinders the catalytic activity owing to CO poisoning. This can cause significant problems for the fuel cells. Palladium is found as a solution to reduce the production of CO.

Carbon black has traditionally been the most common material of choice for fuel cell electrocatalyst supports [1]. The other support materials such as carbon nanotubes [2], graphene [3], metal oxides [4] and hybrid structures like carbon-carbon and carbon-metal oxide have critical importance for catalytic activity [5]. In recent years, it is found that certain metal oxides, such as CeO₂ [6], SnO₂ [7] and Fe₃O₄ [8] can enhance the catalytic activity for formic acid oxidation through synergetic interaction with metals such as Pt or Pd. In this study, Bi₂O₃ was used as a support

material because of being corrosion resistant and durable. Geng et al. reported that Pt/Bi₂O₃ catalyst is tolerant to CO poisoning and has higher electrocatalytic activity for CO oxidation [9]. In another study, Pt/Ru/Bi₂O₃ showed high selectivity toward dehydrogenation and the rate of hydrogen generation is determined [10]. In this study, in order to eliminate CO poisoning problem, it was tried to increase the catalytic activity of Pt nanoparticles over Bi₂O₃ support material.

2. Experimental

2.1. Synthesis of Pt nanoparticles on Bi₂O₃ support

Bi₂O₃ supported Pt catalyst was prepared by using microwave irradiation technique. First, the required amounts of Bi₂O₃ and an aqueous solution of H₂PtCl₆ were added in ethylene glycol and then stirred for 30 min. Then the resulting mixture was operated at 800 W power for 1 min and exposed to microwave energy. The catalyst was washed separately with 300 ml of acetone and 250 ml of distilled



water and centrifuged to remove impurities. Finally, it was dried at 100°C for 12 h.

2.2. Characterization

2.2.1. Physical and electrochemical characterization

Crystal structures of the catalyst and support material were analyzed by using XRD (Rigaku Miniflex) with a $\text{CuK}\alpha$ ($\lambda = 1,5406 \text{ \AA}$) radiation source at a scan rate of $0.6^\circ \text{ min}^{-1}$ in the range of $20\text{--}90^\circ$ (2θ). Scanning electron microscope (SEM) with energy-dispersive X-ray spectroscopy (EDS) was used to identify the surface morphology and elemental analyzes of the catalyst. The functional groups of the obtained $\text{Pt/Bi}_2\text{O}_3$ catalyst were characterized by FTIR. Cyclic voltammetry (CV) experiments were conducted at room temperature using the Pt counter electrode, Ag/AgCl reference electrode and glassy carbon working electrode (area = 0.071 cm^2) in 50 mL 0.5M formic acid and 50 mL 0.5 M H_2SO_4 solutions with 100 mL total volume used as an electrolyte solution for determining formic acid oxidation (FAO) activity. CVs were recorded with a scan rate of 20mV/s. The chronoamperometry was recorded at 0.3V for $\text{Pt/Bi}_2\text{O}_3$ and Pd black catalysts using the same experimental conditions.

3. Results and Discussion

Figure 1 shows X-ray diffraction patterns of 10 wt % $\text{Pt/Bi}_2\text{O}_3$ and that of the reference Bi_2O_3 . The diffraction peaks of Bi_2O_3 were shifted to a lower-angle side with Pt loading. The successive shift of the XRD pattern was partly ascribed to the occupation of interstitial sites in Bi_2O_3 by Pt NPs. All diffraction peaks of bare Bi_2O_3 are assigned to bismite crystallized in monoclinic form corresponding to JCPDS files (No. 41-1449.), namely, $\alpha\text{-Bi}_2\text{O}_3$ [11].

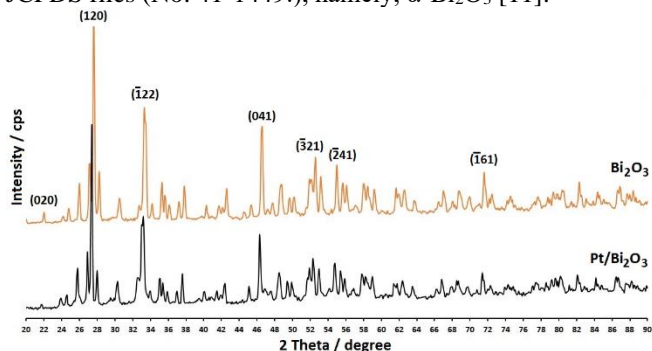


Figure 1. X-ray diffraction patterns of $\text{Pt/Bi}_2\text{O}_3$ and Bi_2O_3

Scanning electron microscope (SEM) images of the $\text{Pt/Bi}_2\text{O}_3$ and the support Bi_2O_3 are given in Figure 2. SEM image in Figure 2a at high magnification shows the densely packed and well-dispersed $\alpha\text{-Bi}_2\text{O}_3$ microrods and Figure 2b shows the Pt clusters on Bi_2O_3 . The size of Pt nanoparticles has increased with increasing microwave irradiation time due to the time-dependent nature of coarsening of particles [12]. The Pt domains show a polydispersity in distributions of size may be due to the increasing reaction time from 3–5 min [13]. On the other hand, a short microwave irradiation time will not be sufficient for the doping of Pt nanoparticles on the surface [14]. For these reasons, 1 min. microwave irradiation time is appropriate for catalyst synthesis. The EDS spectrum (Figure 3) of the $\text{Pt/Bi}_2\text{O}_3$ catalyst contains Pt, Bi and oxygen.

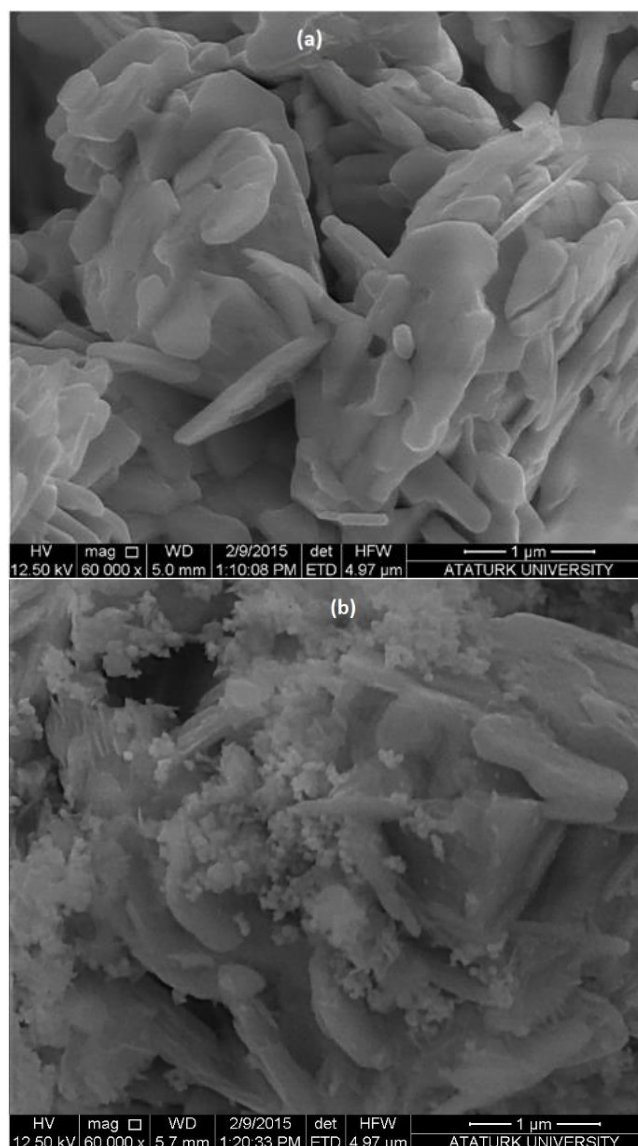


Figure 2. SEM images of the (a) support and (b) $\text{Pt/Bi}_2\text{O}_3$ catalyst

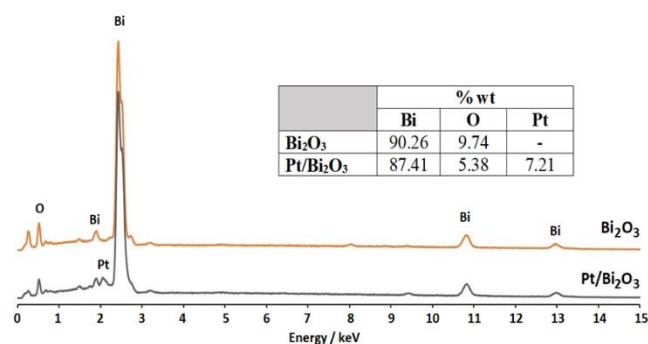


Figure 3. EDS results of Bi_2O_3 and the $\text{Pt/Bi}_2\text{O}_3$

The interaction between pure Bi_2O_3 and Pt doped Bi_2O_3 was studied by FTIR spectroscopy. FTIR spectra were measured in the $4000\text{--}400 \text{ cm}^{-1}$ range. Fig. 4 shows the FTIR spectra of pure and Pt doped Bi_2O_3 . The peak in the region $500\text{--}590 \text{ cm}^{-1}$ appeared in the FTIR spectrum ascribed to the stretching vibration of Bi-O bond for pure Bi_2O_3 [15]. The C-H-stretching modes can be found between 2700 and 3100 cm^{-1} [16]. The intense peaks at 2980 and 2890 cm^{-1} correspond to the asymmetric and symmetric vibrations of CH_2 groups, respectively, of the $\text{Pt/Bi}_2\text{O}_3$ [17]. These C-H stretching modes are probably due to the possible organic molecules available on the surface of the nanoparticles [18].

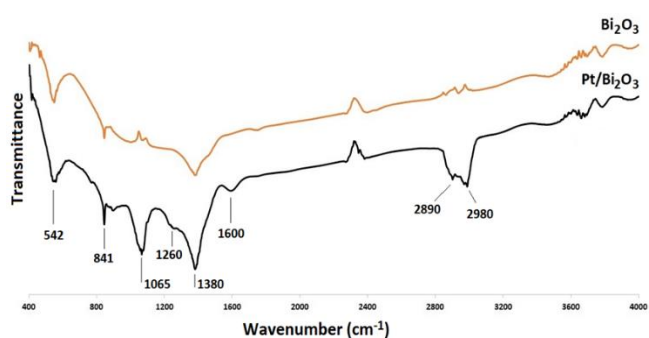
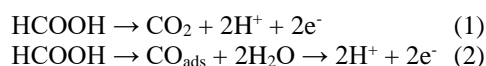


Figure 4. FTIR results of Bi₂O₃ and the Pt/Bi₂O₃

Cyclic voltammetry curves for FAO of Pd black catalyst and Bi₂O₃ supported Pt nanoparticles are shown in Figure 5. It was reported that the electrooxidation of formic acid on catalyst adopts a dual path mechanism, a dehydrogenation path to the direct formation of CO₂ and a dehydration path, and the adsorption of CO intermediate from the dehydration path significantly poisons the activity of Pd catalysts [19]. For the FAO reactions, two peaks were observed in the forward scan. The first peak around 0.30 V results from the direct oxidation of formic acid while the second peak at 0.66 V refers to the indirect path [20]. The reaction mechanisms represented by the following equations [21];



Pt is blocked by adsorbates in the anodic sweep until the onset of CO oxidation. Thus, Pd is more active than Pt under such conditions, but intrinsic activity of Pt is larger and can be partially seen in cathodic sweep after oxidation of CO, or when adsorption of CO is blocked or reduced [22]. Apparently, the Pt/Bi₂O₃ delivers significantly higher electrocatalytic peak current than that of the commercial Pd black.

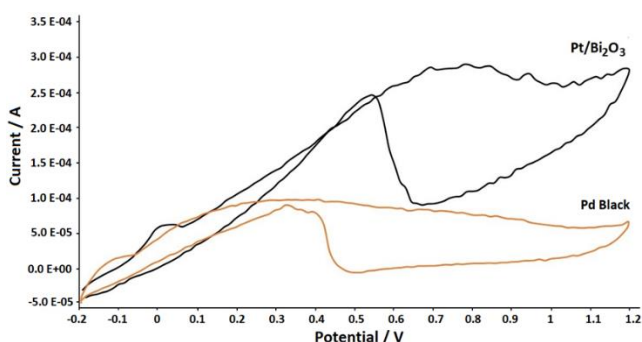


Figure 5. CV results of Pt/Bi₂O₃ and Pd black catalyst

Chronoamperometry for catalytic activity curves were obtained at a fixed potential of 0.3 V for 250 second (Figure 6). Catalyst delivers a similar curve to the results reported in most literature, which drops rapidly at the primary stage and then decays slowly to a limiting value. Obviously, the Pt/Bi₂O₃ exhibits much higher stability than commercial Pd black, which might be contributed from the synergistic effect of Pt nanoparticles and Bi₂O₃ support material.

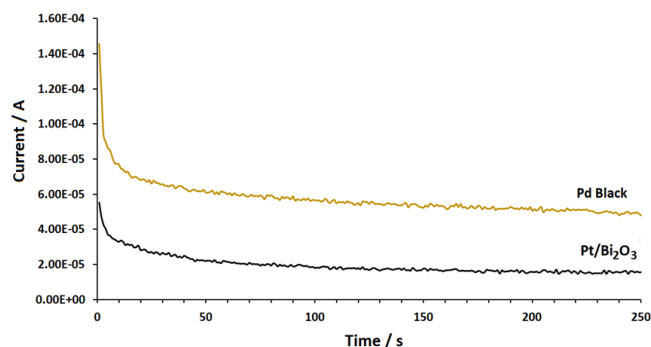


Figure 6. Chronoamperometry results of Pt/Bi₂O₃ and Pd black catalyst

4. Conclusion

Bi₂O₃ supported Pt nanoparticles were synthesized and characterized for possible utilization in FAO. Towards formic acid oxidation, the as-prepared Pt/Bi₂O₃ electrocatalyst exhibits a higher catalytic current and much better stability than the commercial Pd black, thus holding a great promise as a superior anode catalyst in DFAFCs.

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Conflict of Interest

No conflict of interest was declared.

References

- Antolini, E. Carbon supports for low-temperature fuel cell catalysts. *Appl. Catal. B Environ.* **2009**, *88*, 1–24, doi:10.1016/j.apcatb.2008.09.030.
- Caglar, A.; Cogenli, M.S.; Yurtcan, A.B.; Kivrak, H. Effective carbon nanotube supported metal (M=Au, Ag, Co, Mn, Ni, V, Zn) core Pd shell bimetallic anode catalysts for formic acid fuel cells. *Renew. Energy* **2020**, *150*, 78–90, doi:10.1016/j.renene.2019.12.104.
- Çögenli, M.S.; Ayşe, B.Y. Graphene aerogel supported platinum nanoparticles for formic acid electro-oxidation. *Mater. Res. Express* **2018**, *5*, 075513, doi:10.1088/2053-1591/aad0e8.
- An, H.; Cui, H.; Zhou, D.; Tao, D.; Li, B.; Zhai, J.; Li, Q. Synthesis and performance of Pd/SnO₂-TiO₂/MWCNT catalysts for direct formic acid fuel cell application. *Electrochim. Acta* **2013**, *92*, 176–182, doi:10.1016/j.electacta.2012.12.111.
- Cui, Z.; Yang, M.; DiSalvo, F.J. Mo₂N/C hybrid material as a promising support for the electro-oxidation of methanol and formic acid. *Electrochem. commun.* **2013**, *33*, 63–67, doi:10.1016/j.elecom.2013.04.017.
- Ye, L.; Mahadi, A.H.; Saengruengrit, C.; Qu, J.; Xu, F.; Fairclough, S.M.; Young, N.; Ho, P.-L.; Shan, J.; Nguyen, L.; et al. Ceria Nanocrystals Supporting Pd for Formic Acid Electrocatalytic Oxidation: Prominent Polar Surface Metal Support Interactions. *ACS Catal.* **2019**, *9*, 5171–5177, doi:10.1021/acscatal.9b00421.
- Rettenmaier, C.; Arán-Ais, R.M.; Timoshenko, J.; Rizo, R.; Jeon, H.S.; Kühl, S.; Chee, S.W.; Bergmann, A.; Roldan Cuenya, B. Enhanced Formic Acid Oxidation over SnO₂-decorated Pd Nanocubes. *ACS Catal.* **2020**, *10*, 14540–14551, doi:10.1021/acscatal.0c03212.
- Habibi, B.; Ghaderi, S. Electrooxidation of Formic Acid and Formaldehyde on the Fe₃O₄@Pt Core-Shell Nanoparticles/Carbon-Ceramic Electrode. *Iran. J. Chem. Chem. Eng.* **2016**, *35*, 99–112, doi:10.30492/IJCC.2016.23592.
- Geng, J.; Wang, F.; Wu, Y.; Lu, G. The Evidences of Morphology Dependent Electroactivity Toward CO Oxidation over Bismuth Oxide

Supported Pt. *Catal. Letters* **2010**, *135*, 114–119, doi:10.1007/s10562-010-0266-7.

10. Ting, S.-W.; Cheng, S.; Tsang, K.-Y.; van der Laak, N.; Chan, K.-Y. Low activation energy dehydrogenation of aqueous formic acid on platinum–ruthenium–bismuth oxide at near ambient temperature and pressure. *Chem. Commun.* **2009**, 7333, doi:10.1039/b916507j.
11. Li, R.; Chen, W.; Kobayashi, H.; Ma, C. Platinum-nanoparticle-loaded bismuth oxide: an efficient plasmonic photocatalyst active under visible light. *Green Chem.* **2010**, *12*, 212, doi:10.1039/b917233e.
12. Shakoorioskooie, M.; Menciloglu, Y.Z.; Unal, S.; Hayat Soytas, S. Rapid Microwave-Assisted Synthesis of Platinum Nanoparticles Immobilized in Electrospun Carbon Nanofibers for Electrochemical Catalysis. *ACS Appl. Nano Mater.* **2018**, *1*, 6236–6246, doi:10.1021/acsnm.8b01395.
13. Inwati, G.K.; Rao, Y.; Singh, M. In Situ Free Radical Growth Mechanism of Platinum Nanoparticles by Microwave Irradiation and Electrocatalytic Properties. *Nanoscale Res. Lett.* **2016**, *11*, 458, doi:10.1186/s11671-016-1653-9.
14. Şayin, E.S.; Bayrakçeken, A.; Eroğlu, İ. Durability of PEM fuel cell electrocatalysts prepared by microwave irradiation technique. *Int. J. Hydrogen Energy* **2012**, *37*, 16663–16672, doi:10.1016/j.ijhydene.2012.02.170.
15. Raza, W.; Khan, A.; Alam, U.; Muneer, M.; Bahnmann, D. Facile fabrication of visible light induced Bi₂O₃ nanorod using conventional heat treatment method. *J. Mol. Struct.* **2016**, *1107*, 39–46, doi:10.1016/j.molstruc.2015.11.014.
16. Dostert, K.-H.; O'Brien, C.P.; Mirabella, F.; Ivars-Barceló, F.; Schauer mann, S. Adsorption of acrolein, propanal, and allyl alcohol on Pd(111): a combined infrared reflection–absorption spectroscopy and temperature programmed desorption study. *Phys. Chem. Chem. Phys.* **2016**, *18*, 13960–13973, doi:10.1039/C6CP00877A.
17. Sravani, B.; Maseed, H.; Y., C.; Y., V.M.R.; V. V. S. S., S.; Madhavi, G.; L., S.S. A Pt-free graphenaceous composite as an electro-catalyst for efficient oxygen reduction reaction. *Nanoscale* **2019**, *11*, 13300–13308, doi:10.1039/C9NR02912E.
18. Thangamani, C.; Ponnar, M.; Priyadharshini, P.; Monisha, P.; Gomathi, S.S.; Pushpanathan, K. Magnetic Behavior of Ni-Doped CuO Nanoparticles Synthesized by Microwave Irradiation Method. *Surf. Rev. Lett.* **2019**, *26*, 1850184, doi:10.1142/S0218625X18501846.
19. Wang, R.; Wang, H.; Wang, X.; Liao, S.; Linkov, V.; Ji, S. Effect of the structure of Ni nanoparticles on the electrocatalytic activity of Ni@Pd/C for formic acid oxidation. *Int. J. Hydrogen Energy* **2013**, *38*, 13125–13131, doi:10.1016/j.ijhydene.2013.01.104.
20. Pekmez, K.; Sönmez Çelebi, M. Electrooxidation of Formic Acid Using Pt Nanoparticles Supported on Conducting Poly(Vinylferrocene) Polymer Support. *Hacettepe J. Biol. Chem.* **2017**, *3*, 351–358, doi:10.15671/HJBC.2018.175.
21. Maiyalagan, T.; Nassr, A.B.A.; Alaje, T.O.; Bron, M.; Scott, K. Three-dimensional cubic ordered mesoporous carbon (CMK-8) as highly efficient stable Pd electro-catalyst support for formic acid oxidation. *J. Power Sources* **2012**, *211*, 147–153, doi:10.1016/j.jpowsour.2012.04.001.
22. Liang, Z.; Song, L.; Elnabawy, A.O.; Marinkovic, N.; Mavrikakis, M.; Adzic, R.R. Platinum and Palladium Monolayer Electrocatalysts for Formic Acid Oxidation. *Top. Catal.* **2020**, *63*, 742–749, doi:10.1007/s11244-020-01264-5.