Int. J. Electrochem. Sci., 11 **(2016)** 5441 – 5447, doi: 10.20964/2016.07.61

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Electrochemical Synthesis of Bi/Pt Bimetallic Nanodentrites for the Electrooxidation of Methanol

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Received: 18 April 2016 / *Accepted:* 26 May 2016 / *Published:* 4 June 2016

The purpose of this work is to delineate electrooxidation of methanol using hierarchical platinum-bismuth nanodentrites as an electrocatalyst. Potentiostatic electrochemical method was applied to prepare the nanostructures. The shape of nanostructures was controlled by varying the concentration of Pt Cl_6^{2-} ions in fixed Bi^{3+} ions and reaction time. The prepared nanocomposites were characterized by SEM, EDX, XPS and CV techniques. The electrocatalytic activity of Pt–Bi nanodentrites was studied towards methanol oxidation. The prepared nanostructures are simple, eco-friendly and with high electrocatalytic activity.

Keywords: Bismuth, Platinum, nanodentrites, electrochemical method, methanol oxidation

1. INTRODUCTION

Methanol, due to its high efficiency of energy conversion, low operating temperatures and emissions has been used as a fuel in Direct methanol fuel cells (DMFCs)[1-5]. Various complications such as catalyst poisoning owing to the formation of intermediates and methanol diffusion (through the membrane) in methanol oxidation reaction retard the performance of DMFC's[4, 6]. Platinum (Pt) is one of the most active electrocatalyst for the oxidation of methanol in DMFCs[7]. On the other hand, it can be readily poisoned by carbon monoxide species which is strongly adsorbed on platinum active sites during the oxidation of methanol at moderate temperature[7]. The other drawbacks such as high price and sluggish kinetics of Pt also affect the further commercial application of DMFCs[8].

In order to minimize these key issues, Pt nanomaterials have been synthesized and fabricated with other non-precious metals and metaloxides namely, bismuth[9], zinc oxide[10], copper[11], iron[12], cobalt[13], cerium oxide[14] and nickel[15]. Remarkably, Pt-Bi has proved to be the best electrocatalyst for oxidation of methanol in DFCs because the strong affinity between Bi metalloid and Pt results in the formation of stable alloy compound[16-18]. Therefore, several methods for the synthesis of Pt-Bi including chemical, microemulsion, microwave irradiation and electrochemical methods have been developed[18]. This alloy compound exhibits an increase in catalytic activity for methanol oxidation than that of individuals[17]. Moreover, the role of Pt-Bi has also been extended to other applications including electrochemical degradation of methyl orange and oxidation of 1-phenylethanol and pyridinemethanol[19].

In our work, we have electrochemically synthesized Pt-Bi bimetallic nanodentrites through simple electrochemical potentiostatic method and it has been confirmed by various techniques. The prepared nanocomposite has good electrocatalytic activity than that of only Pt/GCE.

2.1 Reagents and apparatus

Potassium hexachloroplatinate (IV), Bismuth (III) nitrate pentahydrate, di sodium ethylene diamine tetra acetate and perchloric acid were purchased from Sigma Aldrich. Prior to each experiment, all the solutions were deoxygenated with pre-purified N_2 gas for 15 min unless otherwise specified. Double distilled water with conductivity of ≥ 18 MΩ cm^{-1} was used for all the experiments.

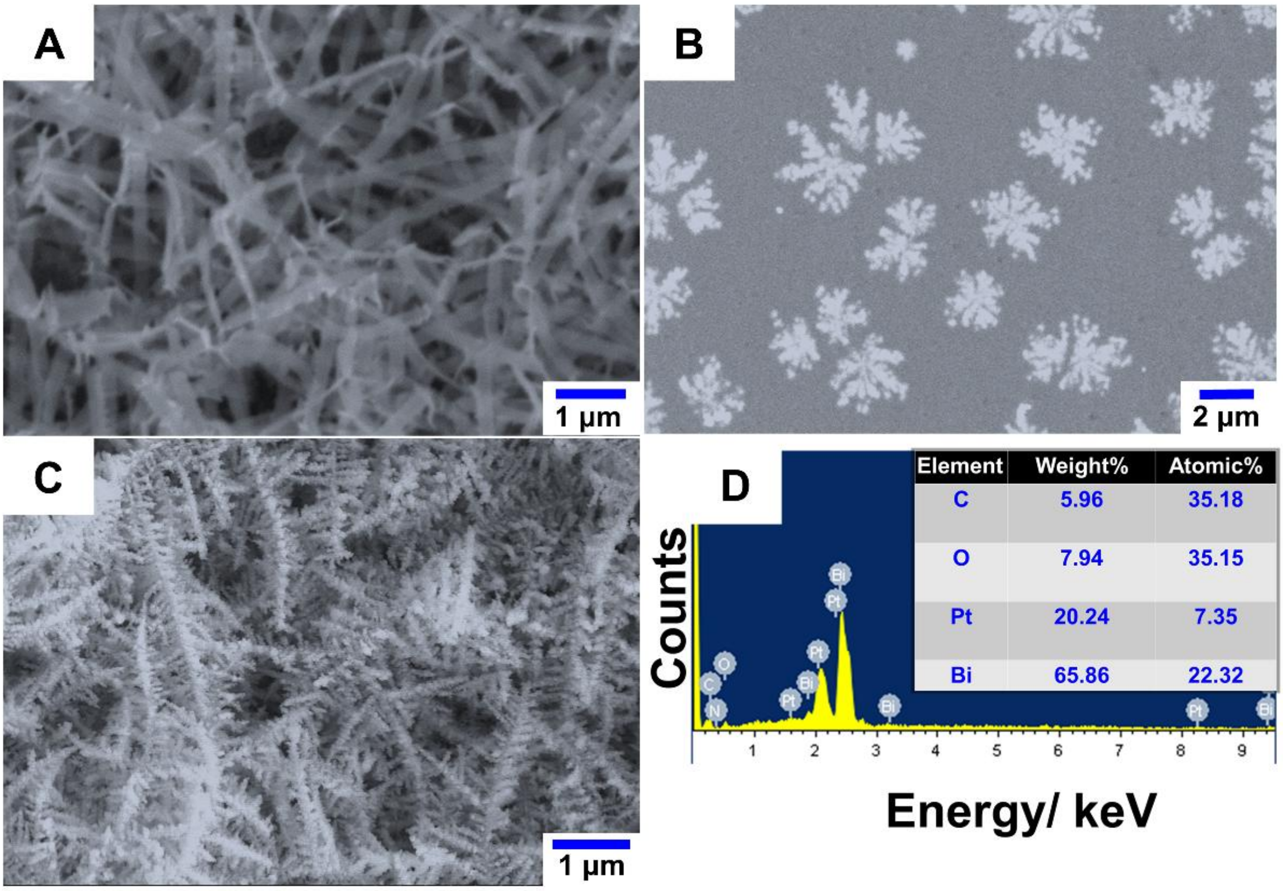
The electrochemical measurements were carried out using CHI 405A electrochemical work station. Electrochemical studies were performed in a conventional three electrode cell using glassy carbon electrode (GCE) as a working electrode (area= 0.071 cm^2), Ag|AgCl (saturated KCl) as a reference electrode and Pt wire as a counter electrode. Scanning electron microscope (SEM) and energy dispersive X-ray (EDX) spectra were performed using Hitachi S-3000H scanning electron microscope and HORIBA EMAX X-ACT, respectively. X-ray photoelectron spectroscopy (XPS) was performed using a PHI 5000 Versa Probe equipped with an Al Ka X-ray source (1486.6 eV).

2.2 Electrodeposition of Pt-Bi nanodentrites on the surface of GCE.

In a typical reaction, 2 mM K_2PtCl_6, 5 mM $Bi(NO_3)_3$ and 10 mM Na_2EDTA were mixed in double distilled water and then sonicated for 10 mins to get the homogenous solution. After sonication, the mixture was transferred in an electrochemical cell. Before performing electrodeposition, the electrodes (GCE, Platinum and Ag|AgCl) were dipped in homogenous solution for 2 min to obtain the equilibrium condition. Then, electrochemical deposition was carried out at a constant applied potential of −1.20 V (vs. Ag|AgCl) on GCE for 15 min. As a control, the similar procedure was used to prepare Bi–NRs/GCE and Pt/GCE.

3. RESULT AND DISCUSSION

3.1 Surface morphological study of Pt–Bi nanocomposite



Element	Weight%	Atomic%
C	5.96	35.18
O	7.94	35.15
Pt	20.24	7.35
Bi	65.86	22.32

Figure 1. SEM images of Bi NRs (A), Pt Ns (B) and Pt-Bi NDs (C). EDX spectrum of Pt-Bi NDs (D)

Scanning electron microscopy (SEM) was used to study the morphology of electrochemically prepared nanocomposites. The SEM image of prepared bismuth shows ribbons like structures (Fig 1A). Whereas, the prepared Pt displays flower like structure (Fig 1B). Hierarchal bimetallic nanodentrites was observed for co-deposited bismuth and platinum film (Fig 1C). This growth of nanodentrites can be due to the capping or chelating agent di sodium ethylene diamine tetra acetate (Na_2EDTA). Moreover, Na_2EDTA is highly hydrophilic which acts as an excellent ligand for of stable complex with metal ions bismuth and platinum in aqueous medium because it has two molecule of water and therefore, it is easy to dissolve in aqueous solution of bismuth and platinum medium than that of other anhydrous form [20]. In addition, the influence of concentration of Pt(IV) precursor with constant concentration of 5 mM Bi(III) ions was studied and their SEM images are displayed in Fig.2 (A–D). Upon increasing the concentration of platinum from 0.5 to 3 mM. The highly dense structure of Pt-Bi nanodentrites was observed at 2 mM concentration of Pt. The increased concentration of Pt (3 mM) affects the growth of Pt-Bi nanodentrites. Therefore, Pt concentration was fixed as 2 mM for the preparation of Pt-Bi nanodentrites. To confirm the elemental and composition of the Pt–Bi NDs, energy dispersive X-ray (EDX) spectroscopy was used. The Fig. 1D portrays the EDX signals of carbon, oxygen, bismuth and platinum with weight percentage of 5.96, 7.94, 65.86 and 20.24.

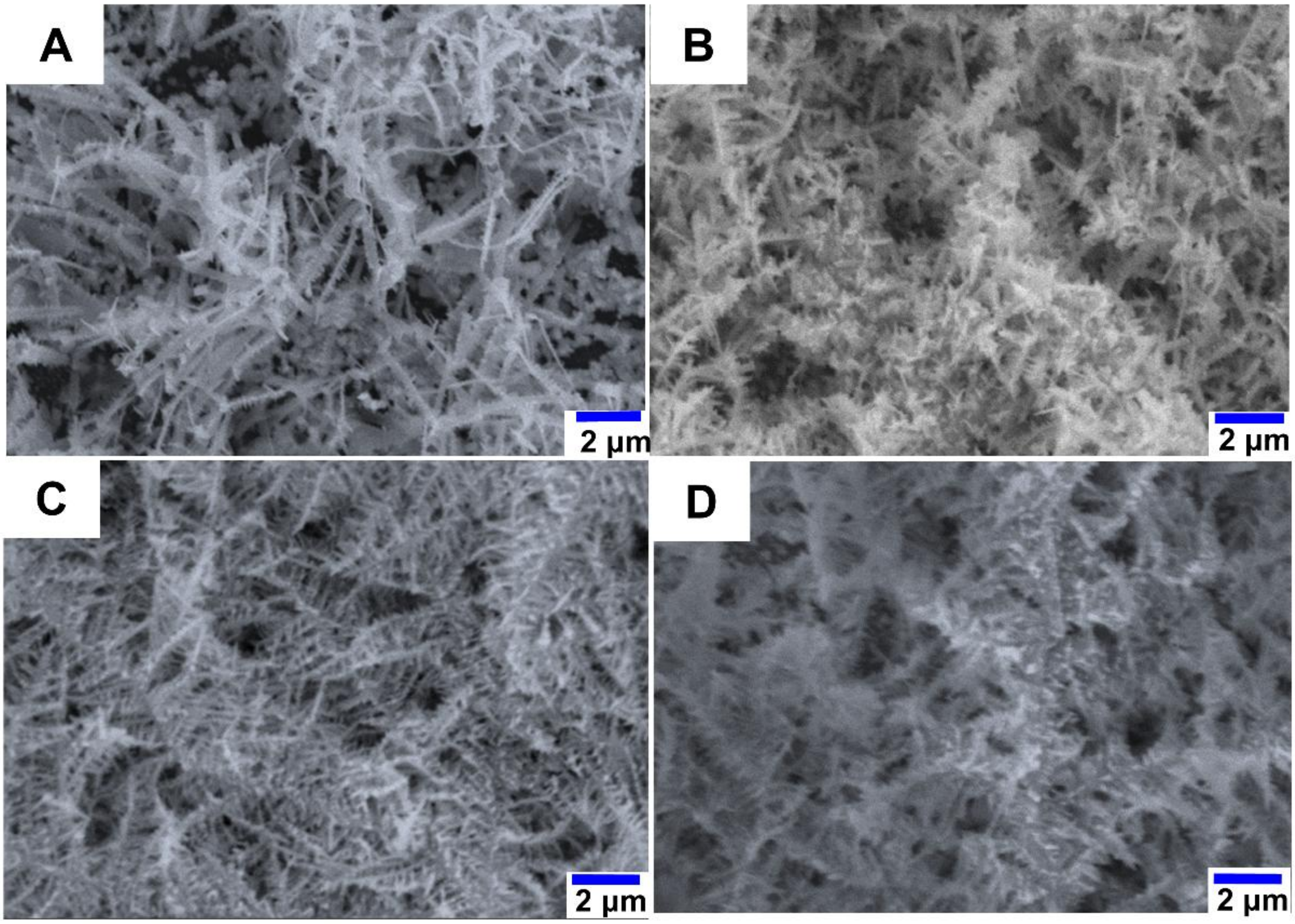


Figure 2. SEM images of Pt-Bi NDs prepared from various concentration 0.5 mM (A), 1mM (B), 2mM (C) and 3 mM (D) of Pt Cl_6^{2-} at fixed concentration of 5 mM Bi^{3+}.

3.2 Surface characterization of the Pt–Bi NDs

XPS spectra was used to study the elemental composition of Pt–Bi nanodentrites in which elements namely, Pt, Bi, C and O were detected in the nanodentrites (Fig 2A). Fig 2B shows the elongated XPS spectra of Pt/Bi BNDs. The binding energies of Pt 4f 7/2, Pt 4f 5/2, Bi 4f 7/2 and Bi 4f 5/2 were appeared at 69.5, 73.0, 157.5 and 163 eV respectively. The obtained results are in concordance with the previously reported Pt–Bi based paper [17]. Moreover, the binding energies of C 1s and O 1s were appeared at 285 and 530 eV respectively which can be from the capping or coordinating agent EDTA. Thus the role of EDTA in the formation of Pt-Bi NDs was confirmed by XPS spectroscopy.

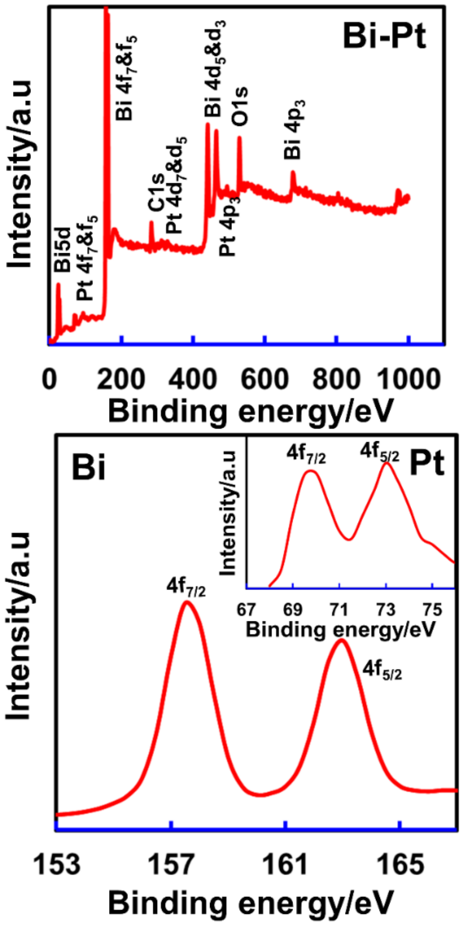


Figure 3. X-ray photoelectron spectroscopy of Pt-Bi NDs**.**

3.3 Electrochemical investigation of Pt–Bi NDs modified GCE towards oxidation of methanol.

The catalytic activity of Pt–Bi NDs (b) and Pt (a) modified GCE was studied by CV method in 0.5 M $HClO_4$ + 0.5 M CH_3OH aqueous solution at the scan rate of 50 mV/s and their results are given in Fig. 4A. Pt–Bi NDs/GCE shows higher catalytic activity towards oxidation of methanol than that of Pt/GCE. Moreover, the onset potential for the oxidation of methanol at the surface Pt–Bi NDs occurs at 0.3 V, which is lower than that of Pt/GCE, indicating that oxidation of methanol is faster at the surface of Pt–Bi NDs. Moreover, the ratio of forward oxidation peaks current (I_f) to the reverse anodic peak current (I_b) is higher than that of Pt/GCE, indicating that it minimizes the poisoning species on the catalyst surface and increase the oxidation of methanol. The performance of our modified electrode towards methanol oxidation was more comparable with the previously reported Pt-Bi modified electrode [16-18].

The influence of scan rate at Pt–Bi NDs/GCE in 0.5 M $HClO_4$ + 2 M CH_3OH was studied. Fig. 4 B shows that the anodic peak currents of methanol oxidation increased with the increase of scan rates. Besides, the potential of modified electrode (Ep) moves linearly to positive direction with an increasing scan rate. This directs that the fabricated Pt–Bi NDs modified GCE modified electrode follows diffusion controlled electrochemical process towards the oxidation of methanol. Fig. 4C displays CVs of Pt–Bi NDs/GCE in the absence (a) and presence of each addition 0.5 M (b to f) of methanol in 0.5 M $HClO_4$ at the scan rate of 50 mV s^{-1}. A enhanched anodic peak (I_p) was obtained upon increasing the concetration of methanol into the electrolyte. This indicates that Pt–Bi NDs/GCE is efficiently catalyse the oxidation of methanol.

Long-term stability of Pt/GCE (a) and Bi–Pt NDs/GCE (b) were studied by chronoamperometric method. The experiment was carried at the potential of 0.8 V in 0.5 M $HClO_4$ + 0.5 M CH_3OH for 1000s. As can be seen in Fig. 4D, the higher current density was observed at Bi–Pt/GCE than that of only Pt/C electrode. Moreover, a slight decay was observed at the Bi–Pt/GCE during the first 150s. It indicates that the intermediate products of methanol oxidation were adsorbed on the surface of the electro catalyst afterwards the current density was reached steady state and remained stable throughout the testing period. This indicates that good durability and tolerance against intermediates of methanol and catalytic ability of Bi–Pt NDs/GCE towards oxidation of methanol.

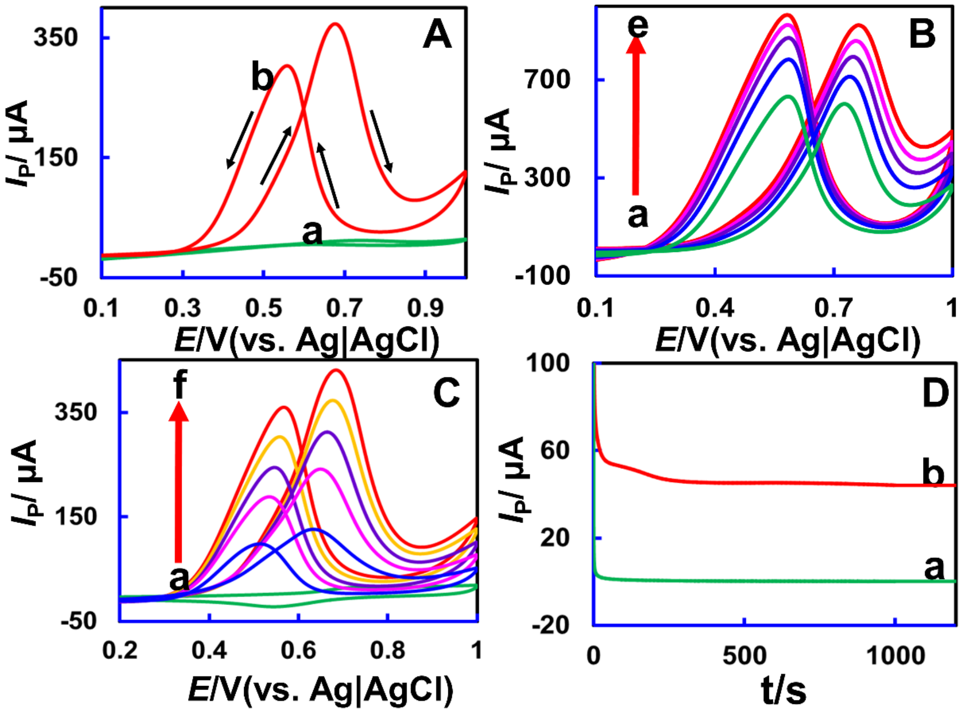


Figure 4. (A) CVs obtained at Pt (a) and Pt–Bi NDs (b) modified GCEs in 0.5 M $HClO_4$ with 0.5 M CH_3OH (scan rate = 50 mV s^{-1}). **(B)** CVs obtained at Bi-Pt NDs in 0.5 M $HClO_4$ with 1 M CH_3OH at different scan rates from 100–500 mV s^{-1}. **(C)** CVs obtained at Pt–Bi NDs in the absence (a) and presence of 0.5 (b), 1 (c), 1.5 (d), 2 (e) and 2.5 M (f) CH_3OH in 0.5 M $HClO_4$ at the scan rate of 50 mV s^{-1}. **(D)** Chronoamperograms of Pt (a) and Pt–Bi NDs (b) modified GCEs at 0.65 V in 0.5 M $HClO_4$+1 M CH_3OH.

4. CONCLUSIONS

We have succesfully prepared Pt–Bi NDs through simple electrochemical potentiostatic method. Morphologies of prepared nanocomposites of prepared nanocomposites were confirmed by SEM. EDX was used to confirm the elecmetal composition of obtained nanocomposites. Surface characterization of nanocomposite was characterized by XPS. The fabricated Pt–Bi NDs modified

GCE exhibited good electrocatalytic acitivity towards oxidation of methanol in terms of higher peak currents and ratio I_f/I_b and tolerence of poisoing intermediates. In addition, the fabricated modified electrode has good durability and stability.

ACKNOWLEDGEMENTS

Dr. Rajkumar Devasenathipathy gratefully acknowledges the National Taipei University of Technology, Taiwan for the postdoctoral fellowship.

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