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Microwave Heated Synthesis of PdAg Core-Shell Nanowires for Electrochemical Oxidation of Ethanol in Alkaline Medium

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Bimetallic electrocatalysts based on Pd such as PdAg, PdNi and PdSn, have shown high efficiencies for ethanol oxidation reaction (EOR). In this study, a novel PdAg core-shell nanowire structure (PdAg-MW) with a Pd:Ag molar ratio of 1:10 was synthesized via a simple two-step process under microwave (MW) pulse mode irradiation in polyol solvent. The effect of MW irradiation time on the formation of Pd shell on Ag nanowires was investigated and compared to the sample PdAg-CP prepared by conventional polyol process. The catalytic ability and stability of the catalysts for ethanol electro-oxidation in KOH solution were examined by using cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronoamperometry (CA) measurements. Tolerance to CO gas was also studied by CO stripping analysis. Surface morphology, structure and composition of the materials were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD) and energy-dispersive X-ray (EDX). The results showed that PdAg-MWs possessed a unique morphology and hollow structure can be achieved at 6-8 times of MW heating. The EOR peak current value is achieved about 3156 mA/mg Pd for PdAg-MW/C, which is superior to Pd nanoparticles/C (PdNPs/C) and PdAg-CP/C, making it a promising Pd-based anodic electrocatalyst for alkaline direct ethanol fuel cells.

1. Introduction

Direct Ethanol Fuel Cells (DEFCs), which can convert directly chemical energy stored in ethanol into electricity (Tahir et al., 2019), have attracted a great deal of attention over two past decades because of its high energy density, low toxicity along with nearly zero-emission (Amin et al., 2014). Most of researches focused on the oxidation of ethanol in alkaline medium have demonstrated that Pd-based nanostructure can be considered as a promising alternative electrocatalyst to Pt-based materials due to its higher efficiency, lower cost and more abundant on earth. The main drawback of DEFCs technology using pure Pd catalyst is the limitation of its commercialization suffered from the high cost of Pd and its poor tolerance of intermediates such as CO formed during the ethanol electrooxidation (Rossetti et al., 2015). Hence, combination Pd with other cheaper metals (Nguyen et al., 2009) such as Ni, Co, Sn, Cu and Ag, especially bimetallic core-shell materials with hollow structures, have emerged as an operative remedy to overcome these issues as well as to enhance the electrocatalytic activity and stability. Among these metals, Ag has achieved an outstanding performance toward ethanol oxidation reaction (EOR) in basic solution when combined with Pd (Nguyen et al., 2009).

The electrocatalytic ability of a catalyst considerably depends on its structure, particle size, morphology, composition and supports. There have been some efforts to evaluate the influence of various nanostructured catalysts on the EOR behaviour of PdAg combination, such as PdAg nanospheres , nano flowers (Bin et al., 2016) and nano dendrites (Jo et al., 2016) . The results showed that applying nano particles in anodic catalysis of DEFCs may cause lower efficiency and stability due to agglomeration suffering from Ostwald ripening effect. Hence 1-D materials have been developed to overcome this limitation.

Colloidal method in polyol solution based on galvanic replacement is widely considered as the most common approach to prepare core-shell materials in nano size. This conventional procedure often undergoes a long

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reaction duration even many days at high temperature and involving many steps including repeated filtering and washing together with lost products, leading to lower yield and higher synthesis cost. Meanwhile, due to rapid and uniform heating, microwave energy can have significant thermal effects on the formation, structure, crystalline degree and morphologies of prepared material with various shapes such as rods, wires, dendrites, sheets.

In this study, Ag NWs were used as the core for the preparation of PdAg core-shell nanowires using MW-assisted polyol method and their electro-catalytic ability towards EOR in KOH solution was tested for the first time.

2. Experimental

2.1 Chemicals

Silver nitrate ($AgNO_3$, 99.0 %), ethylene glycol (EG, 99.5 %), sodium chloride (NaCl, 99.5 %), potassium bromide (KBr, 99.0 %), polyvinylpyrrolidone (PVP, M_w = 40,000), palladium (II) nitrate dehydrate ($Pd(NO_3)_2.2H_2O$, > 99 %), Nafion solution (5 % in isopropanol and water) , Al_2O_3 and ethanol (99.5 %) were purchased from Sigma Aldrich. Vulcan XC-72 carbon black was obtained from Cabot Corp., USA.

2.2 Synthesis procedures

2.2.1 Synthesis of AgNWs

Silver NWs were synthesized by polyol method with ethylene glycol (EG) as a reducing agent. Firstly 10 mL of EG and 0.6251 g of PVP were added to a three necked flask (equipped with a condenser, a thermometer and a magnetic stir bar). The mixture was heated to 150 °C and 0.1 mL of a 0.1 mM KBr solution in EG was injected into the flask. The mixture was stirred for 3 min, then 0.1 mL of a 0.1 mM NaCl solution in EG was added into the solution. Then, 3 mL of 0.4 M $AgNO_3$ in EG was added dropwise into the flask for about 6 min to avoid rapid supersaturation. The reaction temperature was maintained at 150 °C throughout the process. After 120 min, the flask was cooled down to room temperature. Followed by, the sample was diluted with ethanol (at a volume ratio of 1:10) and centrifuged at 3,000 rpm for 20 min to eliminate redundant EG solvent and Ag nanoparticles (if any).

2.2.2 Synthesis of PdAg-CPs via conventional polyol method

PdAg-CPs were synthesized at 70 °C for 150 min to compare to those prepared by MW irradiation. AgNWs prepared in the previous section was dispersed in 10 mL of EG, heated under magnetic stirring until the mixture achieved 70 °C. Two mL of aqueous $Pd(NO_3)_2.2H_2O$ (with a fixed molar ratio of Pd : Ag at 1 : 10 based on initial amount of metal salts) and PVP (at amount of 0.3 wt%) was added dropwise into the reaction flask for 20 min. Then the process was stirred for 150 min. The sample was centrifuged and then dried in a vacuum oven for 24 h at 60 °C.

2.2.3 Synthesis of PdAg-MWs via microwave - assisted polyol method

A domestic microwave oven (Panasonic NN-S215WF, 2450 MHz, 800W) is used to carry out the synthesis of samples. The initial mixture of AgNWs in EG and 2 mL of aqueous Pd $(NO_3)_2.2H_2O$ and PVP were well-dispersed in two separate beakers for 30 min at room temperature. Then the Pd^{2+} solution was added dropwise into the AgNWs solution and stirred for 30 min. The mixture was heated under MW irradiation with pulse mode (10 s on –10 s off) for 6, 8, 10, 12 times. After that, the products were cleaned and dried.

2.2.4 Synthesis of PdNPs

Five mL of EG was heated to 120 °C in a three necked flask (equipped with a condenser, a thermometer and a magnetic stirring bar). Then 0.0243 g $Pd(NO_3)_2$. $2H_2O$ in 2 mL deionized water and 0.0458 g PVP in 3 mL EG were added into the flask simultaneously, and continuous stirring was maintained for 60 min to collect PdNPs.

2.2.5 Catalyst loading on carbon black

The catalyst was mixed with Vulcan XC72 at a mass ratio of 1:4 by stirring in ethanol for 4 h. The mixture was then filtered and dried in vacuum oven at 60 °C for 24 h to obtain the final catalyst supported on carbon, available for physical and electrochemical investigations.

2.3 Characterization

Morphology of samples was investigated using a JEOL 2010 transmission electron microscopy (TEM) operated at an acceleration voltage of 100keV. X-ray powder diffraction was carried out using D8 Bruker AXS X-ray diffractometer (CuKα radiation, 40 kV, 20 mA).

2.4 Electrochemical investigation

The electrocatalytic behaviour of materials for EOR in alkaline media was investigated through cyclic voltammetry (CV) and linear sweep voltammetry (LSV) performance. They all were measured with a Biologic MPG2 potentiostat (France) and a three-electrode cell with a Pt mesh, a saturated calomel electrode (SCE) and a glassy carbon electrode (GCE, 4 mm in diameter) as the counter, reference and working electrode. To prepare working electrode, a GCE was polished with alumina slurry suspension and cleaned with ethanol using ultrasonic bath. The samples for electrochemical tests were prepared by dispersing 3.3 mg of each catalyst in 1 mL ethanol and ultrasonicated for 1 h. Then 5 µL of this well-dispersed suspension was dropped onto GCE using a micropipette. After drying at room temperature, the catalyst was anchored to GCE by dropping 5 µL of 0.5 % Nafion in ethanol onto the catalyst. CV and LSV measurements were conducted in an aqueous solution of (1M KOH + 1M Ethanol) at room temperature at a scan rate of 50 mV/s with potential ranging from -0.8 V to 0.2 V vs SCE. CO stripping process was carried out in 1M KOH solution at room temperature.

3. Results and discussion

3.1 Physical characterization

Morphology and structures of the prepared nanocatalysts were examined with TEM and XRD techniques. The results are presented as below.

3.1.1 TEM results

In the synthesis of silver nanowires, PVP is used as a polymeric capping agent which makes silver particles be confined and directed to grow into nanowires with uniform diameters. Silver nanowires (AgNWs) were formed as shown in Figure 1(a) due to the adsorption of PVP on the (100) planes of Ag seeds, resulting in the anisotropic growth develops along only the (110) direction.

The formation of PdAg core-shell nanowire structure is the result of reaction between Pd^{2+} ions with Ag atoms of AgNWs based on galvanic replacement reaction (GRR). At the same time, Ag atoms are oxidized to Ag^{+} ions, dissolving and producing pinholes on some local surfaces of AgNWs. The growth of Pd nanoparticles forms a layer around AgNWs while the growth of pinholes makes the AgNWs become hollow. As a result, a hollow core-shell material is formed with the Ag core covered with the uniform Pd outer shell.

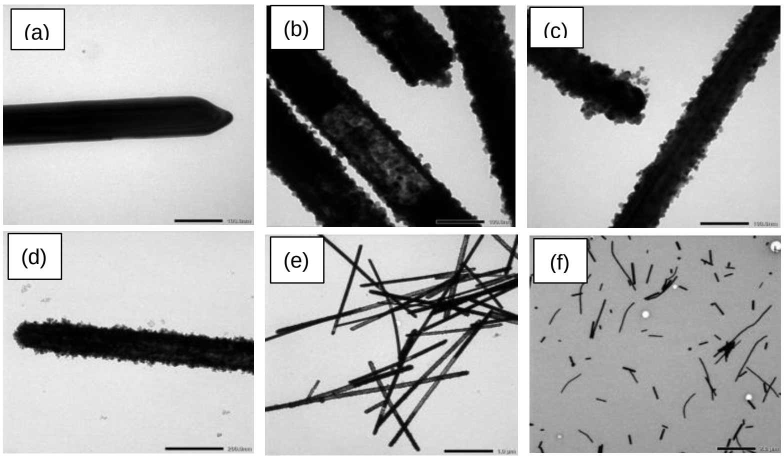

Figure 1: TEM images of: (a) AgNWs (scale bar 100 nm); (b) PdAg-MW6 (scale bar 100 nm); (c) PdAg-MW10 (scale bar 100 nm); (d) PdAg-CP (scale bar 200 nm); (e) PdAg-MW6 (scale bar 1 µm); (f) PdAg-MW12 (scale bar 2 µm).

The morphology of the product is varied when adjusting the number of MW irradiation cycles from 4 to 12 times. TEM results of a series of samples PdAg-MWx (with x= 6, 10 or 12 presenting number of MW irradiation times) in Figure 1 indicate that the morphology of synthesized materials is strongly affected by microwave irradiation. In particular, PdAg-MW6 have a rough surface along with a thin shell of PdNPs on AgNWs. Meanwhile, PdAg-MW10 has a rougher surface with more PdNPs deposited on the AgNWs. They all have "brighter areas" in TEM images, which can be attributed to hollow structure resulted from the dissolving of AgNWs. It can be explained that sufficient energy provision for galvanic replacement occurred facilely with 6 times MW irradiation while further MW supply delivered higher energy leading to higher temperature of reaction system. As a result, PdNPs on the AgNWs surface tend to agglomerate to form larger ones in order to achieve surface-energy-minimization due to Ostwald ripening process as well as nanowire structures are broken into nano rods (Figure 1f).

PdAg-MW6 and PdAg-CP (prepared by conventional polyol method at 70 °C for 150 min) have similar morphology. This proves that instead of lasting for a long time of 150 min reaction, the process can be rapidly carried out about 2 min under MW heating to form nanowire structures of Ag core.

3.1.2 XRD results

XRD patterns of AgNWs/C and PdAg-MW6/C are shown in Figure 2. All the peak positions are in coherence with the standard XRD spectrum of Ag (JCPDS card No. 04-0783) and no peaks of Pd are observed. This indicates that they both possess almost Ag in their composition and the amount of Pd is very small. It can be seen that there is a shift in peak positions of Ag indicating that a partial entrance of Pd atoms into Ag lattice to form PdAg alloy.

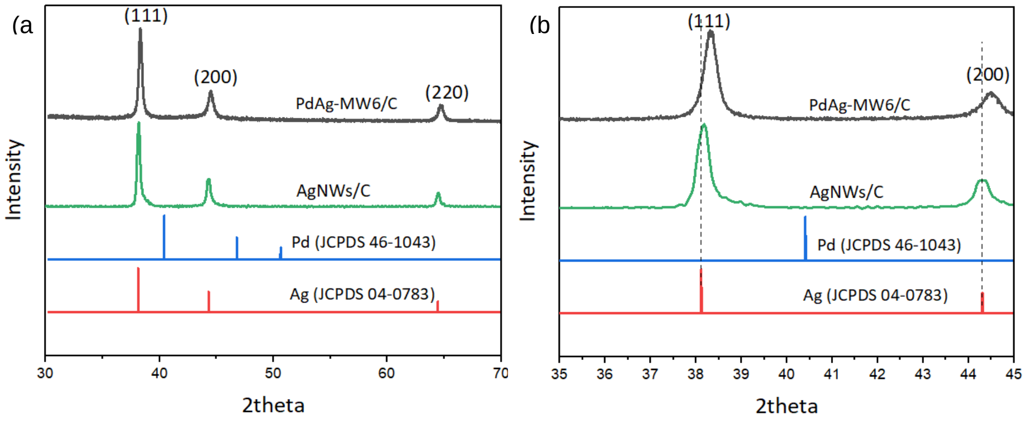

Figure 2: XRD patterns of AgNWs/C and PdAg-MW6/C:(a) from 30 to 70 ° and (b) from 35 to 45°

3.2 Electrocatalytic activity for EOR

Figure 3a shows the cyclic voltammograms (CVs) of PdNPs/C and PdAg-MW6/C in 1 M KOH solution.

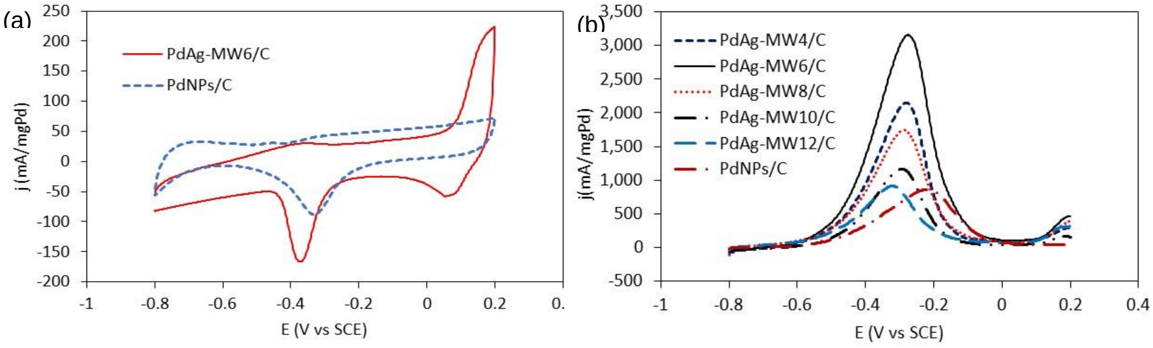

Figure 3: (a) Electrochemical behavior of (a) PdAg-MW6/C and PdNPs/C in 1M KOH solution , (b) PdAg-MWx/C (x=4,6,8,10,12) and PdNPs/C in 1M KOH + 1M C_2H_5OH solution with scan rate 50 mV/s at room temperature.

As can be seen in the forward scan of two samples, a weak peak at around -0.35V can be attributed to the absorption of OH- onto the surface. Meanwhile, for PdAg-MW6/C sample, a strong anodic peak observed at around 0.2V which is disappeared in CVs of PdNPs/C is ascribed to the oxidation of Ag metal to Ag_2O. This is also similar with the backward scan that only peak is existed at around -0.4V is due to the reduction of PdO in PdNPs/C while there is one more peak at 0.15 V in PdAg-MW6/C, relating to the reduction of Ag_2O.

LSV tests were performed to examine the electrocatalytic activity for EOR of samples at various times of MW irradiation (Figure 3(b)). It is clearly observed that the highest catalytic efficiency belongs to PdAg-MW6/C and the lowest one fits to PdAg-MW12/C.

For comparison, CV data are plotted in Figure 4a and details are tabulated in Table 1. It can be seen that the onset potentials of PdAg-MW6/C and PdAg-CP/C are both more negative than that of PdNPs/C (-0.7V, -0.68V and -0.56V). The I_f/I_b ratios of the anodic peak current density (I_f) and the reverse anodic peak current density (I_b) of PdAg-MW6/C and PdAg-CP/C are higher than 1 while PdNPs/C possesses I_f/I_b ratio smaller than 1. The I_f/I_b ratio can be used to evaluate the catalyst tolerance to carbonaceous species accumulation. A higher value of I_f/I_b means the ethanol oxidation process takes place efficiently and the accumulation of intermediate compounds on the electrode surface is low. These results point out that the PdAg core-shell structure not only promote the electro-oxidation of ethanol but also effectively remove the poisoning intermediate compounds formed on the catalyst surface. PdAg core-shell with partly hollow structure can provide two sides (inner and outer surfaces) which can increase active catalytic sites on surface. Besides, Ag in products can improve the adsorption of ion OH^- to form Ag-OH_{ads} which can interact with intermediate compounds like Pd-$(CH_3CO)_{ads}$ and release Pd. In addition, the sample PdAg-MW6/C has the most negative onset potential and highest peak current intensity. It possesses the smoothest surface which preferentially exposes Pd (100) facets having the most active performance towards ethanol oxidation.

Table 1: Electro-catalytic results of PdAg-MW6/C compared to PdAg-CP/C and PdNPs/C

Samples	E_s(V)	I_f(mA/mgPd)	I_b(mA/mgPd)	I_f/I_b
PdAg-MW6/C	-0.70	3,155.95	1,946.01	1.62>1
PdAg-CP/C	-0.68	1,652.75	1,064.32	1.55>1
PdNPs/C	-0.56	860.73	1,546.75	0.56<1

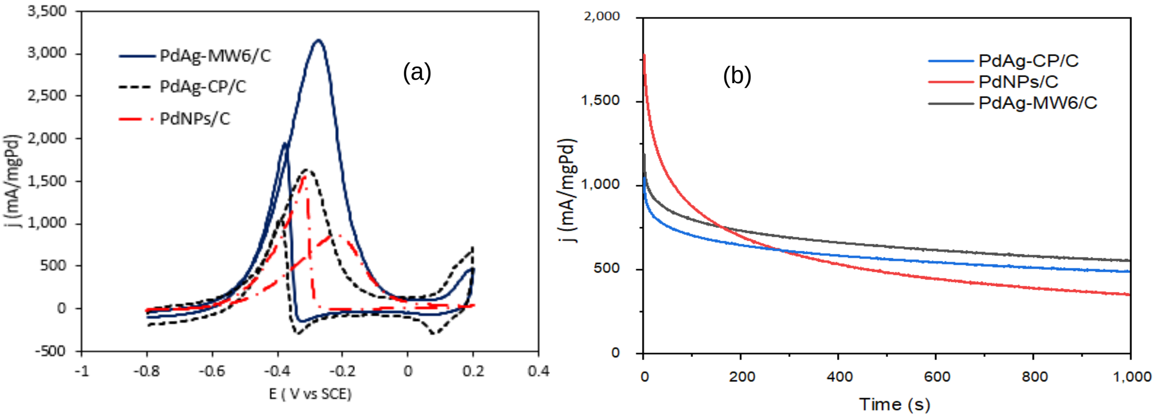

Figure 4: (a) CV results in (1M KOH + 1M C2H5OH) solution with scan rate 50 mV/s and (b) CA results

3.2.1 CA results

CA measurements were carried out at -0.42 V for 1000s in (1M KOH + 1M C_2H_5OH) solution in order to evaluate the catalytic stability. Three CA curves displayed in Figure 4(b) show that the current drops sharply during the first few minutes and then becomes relatively stable. The stability is in order of PdAg-MW6/C > PdAg-CP/C > PdNPs/C proving the good catalytic efficiency for EOR of PdAg core-shell nanowire catalysts prepared with MW irradiation.

3.2.2 CO stripping results

The CO stripping was carried out to investigate the tolerance to CO-intermediate formed during the EOR. Figure 5 shows that PdAg-MW6/C and PdAg-CP/C have more negative onset potentials for CO oxidation compared to PdNPs/C. This result proves the effective of silver’s role in improving the tolerance to CO poisoning of Pd catalysts. In addition, compared to Pd nanoparticles, two peaks for CO stripping observed for PdAg catalysts can be due to the presence of Pd and PdAg alloyed NPs formed on AgNWs.

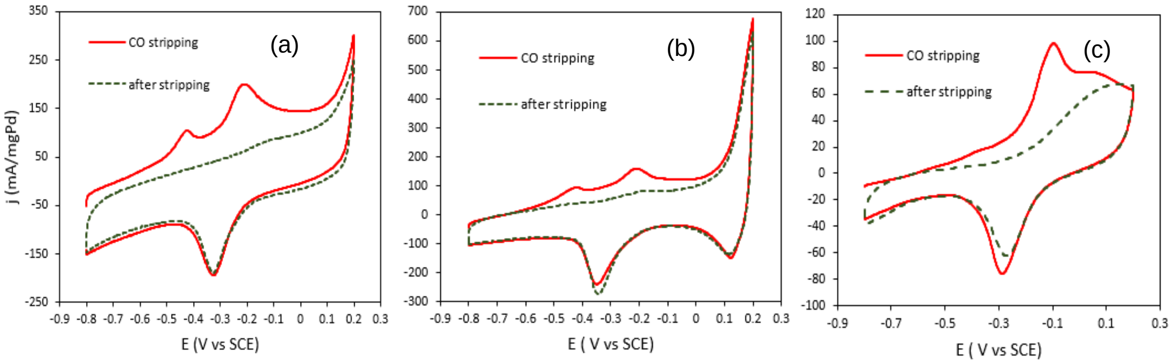

Figure 5: Results of CO stripping: (a) PdAg-MW6/C; (b) PdAg-CP/C and (c) PdNPs/C

4. Conclusion

In conclusion, PdAg nanowires with core-shell structure were synthesized successfully by microwave-assisted polyol method with pulse mode after several cycles of 10 s on -10 s off setting. Further MW irradiation made the nanowires broken into nanorods. The PdAg-MW/C catalysts prepared with microwave irradiation showed higher catalytic ability, durability and CO tolerance for ethanol oxidation reaction compared with PdAg-CP/C prepared by conventional polyol method and PdNPs/C. Taking of such outstanding properties, they can be a suitable candidate alternating to anodic Pt-based catalyst for DEFCs.

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