



理學碩士 學位 論文

Shape-Controlled Pd Nanocrystal-Polyaniline Heteronanostructures with Modulated Polyaniline Thickness for Efficient Electrochemical Ethanol Oxidation (연료전지의 전기화학적 에탄을 산화 효율 증대를 위한 팔라듐 나노결정의 모양 및 폴리아닐린 두께 조절이 가능한 팔라듐-폴리아닐린 복합나노구조체의 합성)

蔚山大學校大學院

化學科

金憲喆

Shape-Controlled Pd Nanocrystal-Polyaniline Heteronanostructures with Modulated Polyaniline Thickness for Efficient Electrochemical Ethanol Oxidation

指導教授홍종욱

이 論文을 理學碩士 學位 論文으로 제출함

2021年 2月

蔚山大學校大學院

化學科

金憲喆

金 憲 喆의 理學碩士 學位 論文을 認准함

審査委員	이 민 형	印
審查委員	홍종욱	印
審査委員	김 범 진	印

蔚山大學校大學院

2021年 2月

국문요약

현재 주요 에너지원으로써 사용되는 화석연료의 경우, 한정된 매장량으로 인해 100년 내에 고갈될 것으로 예상됩니다. 또한, 화석연료의 연소를 통해 많은 환경문제들을 발생시킵니다. 따라서 화석연료를 대체할 수 있는 에너지원의 개발이 필수적이며, 친환경적이고 재생 가능한 에너지원에 대한 많은 연구가 진행되고있습니다.

연료전지는 차세대 에너지공급시스템중 하나로써 촉매작용을 통해 연료를 소모하여 전력을 생산하며, 닫힌계에서 화학적으로 전기에너지를 저장하고 충-방전 상태에 따라 바뀌는 전지에 비해 상대적으로 안정합니다. 다양한 종류의 연료전지 중, 고분자전해질 연료전지(polymer electrolyte membrane fuel cell)는 수소이온을 통과시킬 수 있는 고분자막을 전해질로 사용하여 전력을 생산하는 전류 밀도가 큰 고출력 연료전지로써, 100 ℃ 미만의 저온에서 작동되며 구조가 매우 간단합니다. 또한, 빠른 시동과 응답 특성, 우수한 내구성을 가지고 있으며, 수소 이외에도 메탄올, 에탄올 그리고 천연가스를 연료로 사용할 수 있고 최종 생성물 또한 친환경적으로, 매우 각광받는 에너지 공급 시스템입니다.

고분자전해질 연료전지의 촉매로는 백금이 가장 대표적입니다. 하지만 백금의 경우 높은 시장가격, 낮은 매장량 그리고 일산화탄소 중간체에 의해 쉽게 오염되는 경향이 있어 백금에 비해 비교적 저렴하며 비슷한 성질을 띄는 팔라듐이 대체제로 연구되고 있습니다.

금속 촉매의 활성을 높이는 방법으로는 모양, 조성, 크기 조절 등이 있습니다. 또한, 금속 촉매의 활성을 한층 더 높이며 촉매 반응 동안의 안정성을 높이는 방법으로 고분자를 이용한 금속-고분자 복합구조체 합성이 있습니다.

i

본 연구에서는 팔라듐을 나노크기의 육면체와 팔면체로 각각 합성을 하고 표면에 전도성 고분자인 폴리아닐린을 얇게 둘러 팔라듐-폴리아닐린 복합나노구조체를 합성함으로써 에탄올 산화 효율 및 촉매 반응 동안 안정성을 높였습니다.

주사 전자 현미경과 투과 전자 현미경을 통해 팔라듐-폴리아널린 복합나노구조체의 모양과 아닐린의 농도에 따른 폴리아닐린의 두께 변화를 관찰 하였으며, HAADF-STEM-EDS을 통해 팔라듐 육면체 및 팔면체 표면에 골고루 형성된 폴리아닐린을 확인하였으며. 적외선 분광법을 통해 얇게 둘러싼 물질이 폴리아닐린임을 확인하였습니다. X선 회절 분석법을 통하여 촉매의 fcc 구조를 확인하였으며, X선 광전자 분석법을 통해 팔라듐과 팔라듐-폴리아닐린 복합나노구조체의 전자 거동 차이에 대해 확인하였습니다.

팔라듐-폴리아닐린 복합나노구조체의 대조군으로는 팔라듐 육면체, 팔라듐 팔면체, 상업용으로 판매되는 탄소에 담지된 팔라듐을 선택하였으며, 알칼리성 용액에서의 에탄올 산화 반응의 전기화학적 특성을 확인결과, 상업용 팔라듐과 팔라듐 육면체와 비교하여 크게 향상된 에탄올 산화 효율을 확인하였습니다. 이는 {100}면이 나타내는 효율적인 전기화학적 산화 효율과 더불어 폴리아닐린의 π-π 컨쥬게이션으로 인한 높은 전기 전도도에 기인합니다.

이 연구를 통해 촉매의 모양과 조성의 조절을 통해 전기화학적 에탄올 산화를 향상시켰으며, 친환경적이고 지속가능한 새로운 에너지원 개발에 대한 전략을 제공 할 수 있습니다.

ii

Abstract

For fossil fuels currently used as a major energy source, it is expected to be replicated in 100 years due to limited reserves. In addition, the combustion of fossil fuels causes many environmental problems. Therefore, the development of energy sources that can replace fossil fuels is essential, and many studies are underway for environmentally friendly and renewable energy sources. Fuel cell is one of the promising future energysupplying technologies; in particular, the polymer electrolyte membrane fuel cell (PEMFC) is of special interest because of its high energy density, low operation temperature, and low environmental impact. For commercialization of PEMFC, securement of high electrocatalytic activities accompanying high-stability with various fuel conditions is required. Platinum (Pt) is the most typical catalyst for PEMFC. However high cost, low stability, and poisonous intermediates such as CO are the challenges to be overcome. Accordingly, Palladium (Pd) has been investigated as an alternative because of relatively inexpensive cost compared to Pt, and similar properties via negligible mismatch of atomic structure.

There are various methods to increase the activity of metal catalysts such as shape, size and controlled compositional structure. Moreover, metal-polymer heterostructure inhances not only electrocatalytic property but also durability.

Constructing metal nanocrystal (NC)-polymer heteronanostructures (HNSs) with excellent properties in terms of ethanol adsorption and activation will lead to catalysts with significantly enhanced electrochemical ethanol oxidation reaction (EOR).

Herein, we present a facile and effective synthesis method for shape-controlled Pd NCpolyaniline (PANI) HNSs with various PANI thicknesses, which are achieved by using cubic and octahedral Pd NCs as metal NC seeds. By investigating the electrocatalytic properties of various Pd NC-PANI HNSs and their counterparts, we found that electrocatalytic property of the Pd NC-PANI HNSs highly depends on both the exposed facets of Pd NCs and thickness of the PANI coating. The cubic Pd NC-PANI (Pd_{cube}-PANI) HNSs with cubic Pd NCs and 0.7 nm PANI coating significantly improved electrocatalytic performance for the EOR than the Pd_{cube}-PANI HCNs with different PANI coating thicknesses, octahedral Pd NC-PANI (Pd_{octa}-PANI) HNSs with octahedral Pd NCs, cubic Pd NCs, and commercial Pd/C because of synergistic advantages of the favorable exposed facet and optimal PANI coating thickness.

Index

Korean abstract	······ i
Abstract ·····	······iii
I. Introduction	
II. Experimental Section	
III. Result and Discussion	
IV. Conclusion	
V. Reference ·····	

I. Introduction

The field of environment-friendly and sustainable energy has become drastically important because of the ever-increasing consumption of fossil fuels due to high energy demand.¹⁻³ Fuel cells are one of the promising future energy-supplying technologies; in particular, the polymer electrolyte membrane fuel cell (PEMFC) is of special interest because of its high energy density, low operation temperature, and low environmental impact.^{4, 5} In spite of its tremendous potential as an efficient system to convert chemical energy into electric energy, its practical application is limited by the unsatisfactory performance of the catalysts used in it.^{6, 7} For example, Pt is considered to be the most effective catalyst for PEMFCs. However, poisonous intermediates such as CO are produced during potential operation, and the Pt catalysts are deformed by agglomeration and dissolution, diminishing their active surface catalytic sites and leading to an unfavorable increase in overpotential for catalytic reactions in the PEMFC. In addition, high price and low abundance of Pt hampers its extensive employment in the PEMFC system.

Recently, shape-controlled metal nanocrystals (NCs) are being increasingly used as an efficient platform for PEMFCs.⁸⁻¹² Synthesizing NCs bound by particular facets is an effective strategy for the preparation of PEMFC catalysts because the surface atomic arrangements of NCs have great influence on their catalytic properties. Thus, shape-controlled NCs with effective facets enhance the catalytic activity and stability of PEMFCs by mitigating their limitations.¹³⁻¹⁶ Notably, shape-controlled Pd NCs such as cubic NCs with only {100} facets exhibited remarkable electrocatalytic activities toward electrochemical oxidation reactions in both acidic and alkaline electrolytes,^{8, 17-19} indicating their suitability as a substitute for Pt catalyst. However, despite recent advances in the catalytic performance of PEMFCs by using metal NCs with well-controlled shapes, the fuel cells still have insufficient catalytic activity and stability during catalytic reactions. This is a major limitation for the commercialization of PEMFCs. One of the promising strategies to overcome this limitation is to incorporate conductive polymers into metal NCs for preparing metal NC-polymer nanostructures.^{20, 21} Of various conductive polymers, polyaniline (PANI) has been considered well suited for preparing electrocatalysts because its high electric conductivity originates from π - π conjugation and because it has remarkable stability against deformation during operation.²²⁻²⁵ In addition, PANI can not only modify the electronic structure of metal NCs to promote the

electrooxidation of alcohols, but also trigger the formation of the surface-bound hydroxide ion (OHads) and make possible electrooxidation without the formation of surface poisoning molecules such as CO.^{26, 27} Therefore, metal NC-PANI nanostructures are particularly desirable for various electrooxidation reactions of alcohol. For example, Wang et al. demonstrated that Pd-PANI nanotube array catalysts showed improved electrocatalytic activity for ethanol oxidation reaction (EOR) because of the benefits of coupling Pd and PANI.²⁶ In addition, PANI-decorated Pt/C@PANI catalysts exhibited better electrochemical performance than pristine Pt catalysts in an oxygen reduction reaction.²⁸ Nevertheless, in the aforementioned studies, the nanostructures were primarily produced by using metal NCs with irregular shape and size. Furthermore, the previously reported metal NC–polymer nanostructures lack fine–control of PANI thickness, which is significant to the preparation of active metal NC–PANI electrocatalysts. Against this background, it is desirable to prepare electrocatalysts using metal NC with effective exposed facets and PANI and to study their electrocatalytic performance for developing advanced catalysts for various electrocatalysis.

Herein, we present a facile and effective synthesis method for shape-controlled Pd NC-PANI core-shell heteronanostructures (HNSs) with controllable PANI thickness, which is achieved

by using cubic and octahedral Pd NCs as metal NC seeds. Furthermore, since cubic and octahedral Pd NCs are composed of exclusively {100} and {111} facets, respectively, the successful syntheses of cubic and octahedral Pd NC-PANI HNSs with tunable thickness of the PANI coating can provide an effective platform for understanding the influences of metal surfaces and PANI thickness on catalytic performance. Thus, the proposed method will allow

developing the efficient electrocatalysts for alcohol electrooxidation. The present study demonstrates that the electrocatalytic properties of Pd NC-PANI HNSs toward EOR depend greatly on both, the exposed facets of Pd NCs and the thickness of the PANI coating. It was found that {100}-facet-terminated cubic Pd NC-PANI (Pdcube–PANI) HNSs composed of an ultrathin PANI coating (thickness: 0.7 nm) exhibited the largest electrocatalytic activity and stability for EOR because of the synergistic advantages of the favorable exposed facet and optimal PANI coating thickness.

II. Experimental Section

Chemicals and materials. Sodium tetrachloropalladate (Na₂PdCl₄, 98%), potassium bromide (KBr, \geq 99%), polyvinylpyrrolodone (PVP, Mw 55,000), aniline (\geq 99.5 %), and cetyltrimethylammonium chloride (CTAC, 25 wt% in H₂O) and Nafion[®] perfluorinated resin solution (5 wt%) were obtained from Sigma-Aldrich. Palladium on activated carbon (Pd/C, 20 wt%) and ammonium peroxydisulfate (APS, 98.0%) was obtained from Alfa aesar. Hydrochloric acid (35.0 ~ 37.0%) and potassium hydroxide (KOH, 95.0%) were obtained from Samchun. L-ascorbic acid (AA, 99.5%) was obtained from Daejung. Citric acid (99 %) was obtained from Acros Organic. Other chemicals were reagent grade and deionized water with a resistivity of greater than 18.3 MΩ·cm was used in the preparation of reaction solutions.

Synthesis of cubic Pd NCs. In a typical synthesis of cubic Pd NCs, PVP (105 mg), AA (60 mg), and KBr (600 mg) were dissolved in 8.0 mL of deionized (DI) water, and then the reaction mixture is heated until 80 °C under stirring for 10 min. Subsequently, Na₂PdCl₄ (57 mg) was dissolved in deionized water (3 mL) and then injected into the pre-heated reaction mixture. It maintained at 80 °C for 3 h. The product was washed three times with DI water by centrifugation at 10000 rpm for 20 min.

Synthesis of octahedral Pd NCs. In a typical synthesis of octahedral Pd NCs, citric acid (60 mg) and AA (60 mg) were dissolved in 8.0 mL of deionized (DI) water and mixed with an aqueous CTAC solution (200 mM) of 4 mL. After, the reaction mixture is heated until 100 °C under stirring for 10 min. Subsequently, Na₂PdCl₄ (60 mg) was dissolved in deionized water (3 mL) and then injected into the pre-heated reaction mixture. The solution maintained at 100 °C for 3 h. The product was washed three times with DI water by centrifugation at 10000 rpm for 20 min.

Synthesis of Pdcube-PANI and Pdocta-PANI HNSs. In a typical synthesis of Pd_{cube} -PANI HNSs, 10 mg of cubic Pd NCs anchored on carbon supports (20 wt%), 1 mL of aniline (13.4 mM), 1 mL of HCl (1.1 mM) were subsequently injected into 9 mL of DI water with stirring. Then, the reaction mixture was sonicated for 10 min, followed by kept at 1 °C for 1 h. After that, 1 mL of APS (13.4 mM) was added into the reaction mixture with vigorously stirring. The resultant mixture was kept at 1 °C with stirring for 2 h. The product was washed 2 times by centrifugation at 5000 rpm for 20 min. For Pd_{octa} -PANI HNSs, 10 mg of octahedral Pd NCs

were used instead of cubic Pd NCs. The other synthesis conditions are identical with those for the Pd_{cube} -PANI HNSs. For investigating the polymerization behavior dependent on acidity of reaction mixture, 0, 11 μ M, and 1.1 M of HCl (1 mL) were added instead of 1.1 mM of HCl (1 mL) for employing pH 7, 6, and 1, respectively. For preparing Pd_{cube} -PANI_I, Pd_{cube} -PANI_I, Pd_{cube} -PANI_I, and Pdcube-PANI_{IV} HNSs, 6.7, 26.8, 53.6, and 107.2 mM of aniline (1 mL) were added into reaction mixtures instead of 1 mL of aniline (13.4 mM), respectively.

Characterizations of the samples. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images of the synthesized nanocrystals were obtained on Jeol JEM-2100F and Jeol JSM-7610F, respectively. X-ray diffraction (XRD) measurement were conducted on a Bruker D8 Advance scanning for 2 θ at 10 to 80 degree. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a ThermoFisher K-alpha.

Electrochemical measurements. Electrochemical measurements were conducted in a threeelectrode cell using Bio-logic EC-Lab SP-300. Pt wire and Ag/AgCl (3 M NaCl) were used as counter and the reference electrodes, respectively. All electrochemical data was obtained at room temperature. To prepare the working electrode, a 10 μ L of the catalyst ink containing 1 μ g of Pd based on Inductively coupled plasma-optical emission spectrometry (ICP-OES) was dropped onto a glassy carbon electrode (GCE, diameter: 5 mm), and then dried at room temperature. The dried GCE was cleaned electrochemically by 50 potential cycles between -0.85 and 0.35 V vs Ag/AgCl at a scan rate of 50 mV s⁻¹ in 0.1 M KOH. The electrolyte solutions were purged with N₂ gas for 30 min before performing electrochemical experiments. The CVs of all catalysts were obtained between -0.85 and 0.35 V vs Ag/AgCl at a scan rate of 50 mV s⁻¹ in 0.1 M KOH or 0.1 M KOH + 0.5 M ethanol. For CO-stripping experiments, the surface of the catalysts loaded on GCE was saturated with CO by purging CO gas in 0.1 M KOH while holding the working electrode at -0.3 V versus Ag/AgCl for 15 min, and then CO dissolved in electrolyte was removed by purging with N₂ gas for 30 min. The CO stripping experiments were performed between -0.85 and 0.35 V vs Ag/AgCl at a scan rate of 20 mV s⁻¹. **Characterizations**. TEM and SEM images of the prepared catalysts were obtained by using Jeol JEM-2100F and Jeol JEM-7210F, respectively. FTIR measurement was performed by using an IRAffinity-1S (SHIMADZU). ICP-OES measurement was carried out using a Spectroblue-ICP-OES (Ametek). X-ray diffraction (XRD) measurement were conducted on a Rigaku D/MAX2500V/PC. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a ThermoFisher K-alpha.

III. Result and Discussion

To synthesize Pd_{cube} -PANI HNSs, cubic Pd NCs with an average edge length of 17.9 ± 0.6 nm (Fig. 1a) were first produced by reduction of disodium tetrachloropalladate (Na₂PdCl₄) in an aqueous solution containing polyvinylpyrrolidone (PVP), ascorbic acid (AA), and potassium bromide (KBr) (see the Experimental details), which were used as seed NCs for the preparation of Pd_{cube}–PANI HNSs. Subsequently, the cubic Pd NCs were anchored on carbon supports (Fig. 1b). Then, Pd_{cube}-PANI HNSs were obtained by surface-initiated polymerization of aniline on the cubic Pd NCs attached on the carbon supports, as shown in Scheme 1.

The typical transmission electron microscopy (TEM) image of the Pd_{cube}-PANI HNSs shown in Fig. 2a shows that cubic nanostructures are highly monodispersed on carbon supports. The single crystalline nature of the products is observed in a high-resolution TEM (HRTEM) image of an individual nanostructure (inset of Fig. 2b), and the measured average thickness of the PANI coating is 0.7 ± 0.1 nm. The d-spacing of adjacent lattice fringes along the edge of the cubic NC is 1.95 Å, which matches well with that of the {200} planes of face-centered cubic (fcc) Pd.²⁹ This corroborates that the exposed surfaces of cubic NCs of the Pd_{cube}-PANI HNSs are {100} facets, which are further confirmed from the fast Fourier transform (FFT) pattern viewed along the [001] zone axis (inset of Fig. 2b). Fig. 2c presents the X-ray diffraction (XRD) pattern of the Pdcube-PANI HNSs indexed to the fcc Pd crystalline structure. The cubic shape of the product is also clearly confirmed from a high-angle annular dark-field scanning TEM (HAADF-STEM) image (Fig. 2d). For examining the composition of the Pd_{cube}-PANI HNSs, an elemental mapping image was obtained by HAADF-STEM-energy-dispersive X-ray spectroscopy (HAADF-STEM-EDS). The intense nitrogen (N) signals observed around a cubic Pd NC and carbon supports indicate the formation of a PANI coating layer on the surfaces of cubic Pd NCs attached on the carbon supports (Fig. 2d). To further verify the formation of the PANI coating on the cubic Pd NCs, we obtained the Fourier transform IR (FTIR) spectra of the Pd_{cube}-PANI HNSs and pristine polyaniline (Fig. 3). The FTIR spectrum of the Pd_{cube}-PANI HNSs reveals distinctive characteristic peaks such as those of amide (710 cm⁻¹), aromatic amine (1135 cm⁻¹), carbonyl groups (1650 cm⁻¹), which correspond to PANI.^{22, 23, 25, 30} This observation implies that the surface of Pd NCs was covered with PANI.



Scheme 1. Schematic illustration for the formation of Pd-PANI HNSs.



Fig. 1. TEM images of (a) cubic Pd NCs, (b) cubic Pd NCs on carbon support.



Fig. 2. (a) Low- and (b) high-magnification TEM images of Pd_{cube} -PANI HNSs. The insets in Fig. 2b show the visible lattice fringes and an FFT pattern obtained from a cubic Pd NC in the Pd_{cube} -PANI HNSs, respectively. (c) XRD pattern of Pd_{cube} -PANI HNSs. (d) HAADF-STEM and corresponding HAADF-STEM-EDS elemental mapping images of Pd_{cube} -PANI HNSs.



Fig. 3. FTIR spectra of Pd_{cube}-PANI HNSs, Pd_{octa}-PANI HNSs, and PANI.

The procedure for synthesizing octahedral Pd NC-PANI (Pd_{octa} -PANI) HNSs is identical to that for Pd_{cube} -PANI HNSs, except for the introduction of octahedral Pd NCs with an average edge length of 21.3 ± 0.7 nm (Fig. 4a,b) instead of cubic Pd NCs in the former (Scheme. 1). As seen in the TEM image (Fig. 5a), the octahedral NCs are clearly shown in a majority of products. The HRTEM image of an octahedral NC in Pd_{octa} -PANI HNS reveals their high crystallinity (inset of Fig. 5b). The thickness of the PANI coating is 0.7 ± 0.1 nm. The d-spacing of 2.25 Å between adjacent lattice fringes matches well with that of the {111} planes of fcc Pd, indicating that the {111}-facet-bounded octahedral Pd NCs are included in the Pd_{octa}-PANI HNSs (Fig. 5b).³¹ The XRD patterns of the Pd_{octa}-PANI HNSs display the characteristic diffraction peaks seen in the reflections of the fcc Pd crystalline nature of the prepared Pd-PANI HNSs (Fig. 5c). The HAADF-STEM and HAADF-STEM-EDS mapping images of the Pd_{octa}-PANI HNSs (Fig. 5d). Moreover, similar to Pd_{cube}-PANI HNSs, distinct intrinsic peaks corresponding to PANI were also observed in the FTIR spectrum of the products (Fig. 3).



Fig. 4. TEM images of (a) octahedral Pd NCs, and (b) octahedral Pd NCs on carbon support



Fig. 5. (a) Low- and (b) high-magnification TEM images of Pd_{octa} -PANI HNSs. The insets in Fig. 5b show the visible lattice fringes and an FFT pattern obtained from an octahedral Pd NC in the Pd_{octa} -PANI HNSs, respectively. (c) XRD pattern of Pd_{octa} -PANI HNSs. (d) HAADF-STEM and corresponding HAADF-STEM-EDS elemental mapping images of Pd_{octa} -PANI HNSs.

Given that the acidity of the reaction mixture for producing metal NC-polymer nanostructures greatly influences the polymerization behavior and deformation of metal NCs during polymerization,^{32, 33} employing the optimal acidity is critical to synthesizing metal NCpolymer nanostructures with the desired morphology. The control experiments, wherein the HCl concentration gradually increased under otherwise identical conditions for Pd_{cube}-PANI and Pd_{octa}-PANI HNSs, were conducted to verify the significance of acidity of the reaction mixture (see the Experimental details). When reaction mixtures with pH 6 and 7 were prepared, which have lower acidities compared with the standard condition (pH 4), a negligible PANI coating was observed on the Pd surfaces (Fig. 6a-d). This can be attributed to the predominant formation of the oligomers by the mixed ortho-para coupling than the polymerization of aniline for PANI under pH higher than 434; this can hamper the growth of PANI on the surface of Pd NCs. On the other hand, well-defined PANI coatings with very low thickness of $0.7 \pm$ 0.1 nm were obtained under the standard condition of pH 4 (Fig. 6e,f). However, severe deformation of cubic Pd NCs was observed in the reaction mixture with pH 1 (Fig. 6g,h). This is attributed to the promoted oxidative etching due to the presence of excessive HCl in the reaction mixture.³⁵⁻³⁷ These results clearly show that the acidity of the reaction mixture highly influences the formation behavior of metal NC-polymer nanostructures. We found that an acidity of around pH 4 is appropriate to produce Pd-PANI HNSs without deformation of Pd NCs.



Fig. 6. (a,c,e,g) Low- and (b,d,f,h) high-magnification TEM images of products synthesized under pH (a,b) 7, (c,d) 6, (e,f) 4, and (g,h) 1.

Considering these results, we could control the thickness of the PANI coating of the Pd-PANI HNSs by using different amounts of aniline. Fig. 7 shows the various Pd_{cube} -PANI HNSs with PANI coatings of different thicknesses. Compared to an aniline concentration of 1.22 mM for standard Pd_{cube} -PANI HNSs with a PANI coating of 0.7 ± 0.1 nm (Fig. 7a,a'), Pd_{cube} -PANI_I HNSs with thinner PANI coatings of 0.5 ± 0.1 nm were formed when less amount of aniline (0.67 mM) was used (Fig. 7b,b'). In contrast, Pd_{cube} -PANI HNSs with thicker PANI coatings (1.4 ± 0.2, 1.9 ± 0.2, and 2.7 ± 0.1 nm) were produced for Pd_{cube} -PANI_{II}, Pd_{cube} -PANI_{III}, and Pd_{cube} -PANI_{IV} HNSs, respectively, by injecting 2.44, 4.87, and 9.75 mM of aniline, respectively (Fig. 7c-e).



Fig. 7. TEM images of (a, a') standard Pd_{cube} -PANI, (b, b') Pd_{cube} -PANI_I, (c, c') Pd_{cube} -PANI_{II}, (d, d') Pd_{cube} -PANI_{III}, and (e, e') Pd_{cube} -PANI_{IV} HNSs.

Considering that previous studies the electrochemical oxidation have shown that pure PANI exhibits negligible electrocatalytic activity toward EOR,³⁸ the surface Pd atoms in Pd-PANI HNSs can be presumed as catalytic active sites for EOR. This signifies that an appropriate thickness of PANI coating, which can not only efficiently facilitate the migration of chemicals to the Pd surface, but also make possible obtaining the full benefits of the Pd NC-PANI combination, effectively improves their catalytic performance. Accordingly, investigating the optimal thickness of PANI coating is significant for designing the efficient Pd-PANI HNSs for electrocatalysis. To find the optimal thickness of PANI coating, the EOR activities of various Pdcube-PANI HNSs with different PANI coating thicknesses, standard Pdcube-PANI, Pdcube-PANII, Pdcube-PANIII, Pdcube-PANIIII, and Pdcube-PANIIV HNSs, were evaluated in an alkaline electrolyte. The current densities obtained in cyclic voltammograms (CVs) were normalized based on the mass of the catalysts loaded on a glassy carbon electrode (GCE) used as a working electrode. Fig. 8 shows that standard Pd_{cube}-PANI HNSs exhibited the highest mass activity of 1472.6 mA mg⁻¹, which is substantially higher than the mass activities of Pd_{cube}-PANI_I (790.6 mA mg⁻¹), Pd_{cube}-PANI_{II} (480.9 mA mg⁻¹), Pd_{cube}-PANI_{III} (153.6 mA mg⁻¹), and Pd_{cube}-PANI_{IV} (84.1 mA mg⁻¹). As expected, this indicates that the EOR activity of Pd-PANI HNSs is highly dependent on their PANI coating thickness. Plotting the obtained EOR activities as a function of the PANI coating thickness results in a volcano curve according to the mass activities of the different Pd-PANI HNSs (Fig. 8b). As the PANI thickness decreased from 2.7 to 0.7 nm, there was a gradual enhancement of the EOR activities, whereas much thinner PANI coatings (0.5 nm) of Pd_{cube}-PANI_I HNSs had attenuated electrocatalytic activity. These results reveal that the reduction of PANI coating thickness can lead to enhanced electrocatalytic activity, which is attributed to the improved mass transfer of the reaction species; however, excessively thin PANI coating (<0.7 nm) worsens the electrocatalytic activity by attenuating the intrinsic positive benefits of PANI. On the basis of these findings, Pdcube-PANI and Pdocta-PANI HNSs with a PANI coating 0.7 nm thick obtained from the standard syntheses were chosen for further electrochemical investigation.



Fig. 8. (a) CVs obtained with various Pd_{cube} -PANI HNSs with different PANI coating thicknesses in 0.1 M KOH + 0.5 M ethanol. (b) Plot of the obtained EOR activities as a function of the PANI coating thickness. (c) CVs obtained with various catalysts in 0.1 M KOH + 0.5 M ethanol. (d) Catalytic activities of various catalysts.

To explore the influence of the surface morphology of Pd NCs and formation of the PANI coating on the catalytic activity of catalysts, the electrocatalytic properties of the Pd_{cube}-PANI and Pdocta-PANI HNSs were estimated, and the results were compared with those of cubic Pd NCs and commercial Pd/C catalysts. Fig. 9a shows the CVs of different catalysts in N₂saturated 0.1 M KOH. The electrochemically active surface areas (ECSAs) of the nanostructures obtained from the charge required for oxygen species desorption in the CVs of the nanostructures were 33.0, 29.3, 23.2, and 47.9 m² g⁻¹ for the Pd_{cube}-PANI HNSs, Pd_{octa-} PANI HNSs, cubic Pd NCs, and Pd/C catalysts, respectively (Fig. 9b). Fig. 8c shows the CVs obtained for the EOR with different catalysts in 0.1 M KOH and 0.5 M ethanol. It is apparent that the Pd_{cube}-PANI HNSs showed the highest EOR activity among the different catalysts. The mass activity of the Pd_{cube}-PANI HNSs (1472.6 mA mg⁻¹) is roughly 3.7, 2.1, and 2.1 times higher than those of the Pd_{octa}-PANI HNSs (402.9 mA mg⁻¹), cubic Pd NCs (707.1 mA mg⁻¹), and commercial Pd/C (697.9 mA mg⁻¹) catalysts, respectively (Fig. 8d). Furthermore, the corresponding current density of the Pd_{cube}-PANI HNSs was 4.46 mA cm⁻², which is roughly 3.3, 1.5, and 3.1 times higher than those of the Pd_{octa}-PANI HNSs (1.35 mA cm⁻²), cubic Pd NCs (3.07 mA cm⁻²), and commercial Pd/C (1.43 mA cm⁻²) catalysts, respectively (Fig. 10).



Fig. 9. (a) CVs of the Pd_{cube}-PANI HNSs, Pd_{octa}-PANI HNSs, cubic Pd NCs, and commercial Pd/C in 0.1 M KOH at a scan rate of 50 mV s⁻¹ and (b) corresponding ECSAs of different catalysts.



Fig. 10. (a) CVs of the Pd_{cube}-PANI HNSs, Pd_{octa}-PANI HNSs, cubic Pd NCs, and commercial Pd/C in 0.1 M KOH + 0.5 M ethanol at a scan rate of 50 mV s⁻¹ and (b) corresponding catalytic activities of different catalysts

The electrochemical stability of Pd_{cube} -PANI HNSs was evaluated via accelerated durability test (ADT) and compared with those of Pd_{octa} -PANI HNSs, cubic Pd NCs, and commercial Pd/C catalysts. During the measurements, the catalysts loaded on a working electrode were applied between -0.85 and 0.3 V in N₂-saturated 0.1 M KOH and 0.5 M ethanol. After 500 cycles, the Pd_{cube}-PANI HNSs, Pd_{octa}-PANI HNSs, cubic Pd NCs, and commercial Pd/C catalysts exhibited 1113.0, 286.5, 379.8, and 349.7 mA mg⁻¹, respectively, which signifies losses of 24.4, 28.9, 46.3, and 49.9% in mass activity, respectively (Fig. 11). The superior catalytic stabilities of the Pd_{cube}-PANI and Pd_{octa}-PANI HNSs arise from the PANI coating because the coating can effectively reduce the shape-deformation of the Pd NCs in the Pd_{cube}-PANI and Pd_{octa}-PANI HNSs. Indeed, the TEM images of Pd-PANI HNSs such as Pd_{cube}-PANI and Pd_{octa}-PANI HNSs obtained after 500 cycles show that their initial morphologies were well preserved (Fig. 12a,b), while cubic Pd NCs and Pd/C catalysts underwent shape deformation (Fig. 12c,d).



Fig. 11. CVs obtained before and after ADT for (a) Pd_{cube} -PANI HNSs, (b) Pd_{octa} -PANI HNSs, (c) cubic Pd NCs, and (d) Pd/C catalysts in 0.1 M KOH + 0.5 M ethanol at scan rate of 50 mV s⁻¹. (e) Normalized current density and (f) Mass activities of various catalysts before and after ADT.



Fig. 12. TEM images for (a) Pd_{cube}-PANI HNSs, (b) Pd_{octa}-PANI HNSs, (c) cubic Pd NCs, and (d) Pd/C catalysts after ADT (500 cycles).

The significantly enhanced catalytic activity and stability of Pd_{cube}-PANI HNSs can be attributed to the synergistic effects of the formation of the PANI coating and the Pd{100} facets. Notably, the Pd_{cube}-PANI HNSs in close contact with the cubic Pd NC and PANI coating showed improved catalytic performance for EOR than cubic Pd NCs. This may be a result of the modification of the electronic structure of Pd surface atoms through the delocalization of electrons in the Pd-PANI HNSs. To elucidate the change in the electronic structure of surface Pd atoms in the Pd_{cube}-PANI HNSs, X-ray photoelectron spectroscopy (XPS) measurement on the Pd 3d core-level was conducted with the Pd_{cube}-PANI HNSs and cubic Pd NCs. Fig. 13 shows the negative shift in the binding energies of the Pd_{cube}-PANI HNSs compared with those of pure cubic Pd NCs. For instance, the Pd 3d_{3/2} and Pd 3d_{5/2} binding energies of the Pd_{cube}-PANI HNSs are 341.15 and 335.90 eV, respectively, while those of the cubic Pd NCs are 341.55 and 336.20 eV, respectively. The modified electronic structure of Pd in Pd_{cube}-PANI HNSs may provide the optimal bonding strength between surface-bound COCH₃ ((COCH₃)_{ads}) and surface Pd atoms of the Pd_{cube}-PANI HNSs. This results in enhanced electrocatalytic activities toward EOR because the decomposition of (COCH₃)_{ads} is a ratedetermining step in the electrochemical ethanol oxidation pathway.^{39,40} In addition, it is widely accepted that surface-bound OH (OH_{ads}) on the surface of catalysts can promote EOR by reacting with (COCH₃)ads.⁴¹⁻⁴³ PANI can sufficiently provide OH_{ads} to the surface Pd atoms bound to COCH3 owing to its high OHads formation ability and thus enhance the catalytic activity of the Pd-PANI HNSs.^{26, 27} On the other hand, despite the similar electronic structures of the Pd_{cube}-PANI and Pd_{octa}-PANI HNSs as seen from the XPS measurement (Fig. 13), through the electrocatalytic experiments, we found that the Pdcube-PANI HNSs had larger EOR activities than Pd_{octa}-PANI HNSs.



Fig. 13. XPS spectra for the Pd 3d core-level for (a) Pdcube-PANI HNSs, (b) cubic Pd NCs, and (c) Pdocta-PANI HNSs.

For investigating the higher catalytic activity of the Pd_{cube} -PANI HNSs compared to the Pd_{octa} -PANI HNSs, CO-stripping voltammograms of the catalysts were obtained. Fig. 14 shows that onset potential of the Pd_{cube} -PANI HNSs for the oxidative removal of CO to CO₂ is more negative than that of the Pd_{octa} -PANI HNSs, demonstrating the enhanced CO tolerance of the Pd_{cube} -PANI HNSs resulting from the facile elimination of CO on the $Pd\{100\}$ surfaces. In addition, previous studies on the electrooxidation reactions revealed that $Pd\{100\}$ facets exhibited higher electrooxidation performance than other low-index facets.^{19, 44, 45} This is because of the stronger interatomic interaction of $Pd\{100\}$ facet than $Pd\{111\}$ and $\{110\}$ facets.⁴⁶ These findings collectively corroborate that the types of surface facets are a significant factor that determine the EOR property of electrocatalysts.



Fig. 14. CO stripping measurements of Pd_{cube} -PANI and Pd_{octa} -PANI HNSs.

IV. Conclusion

In summary, various PANI coated Pd_{cube} -PANI HNSs have been successfully produced via a facile wet-chemical method. Introduction of appropriate acidity is a pivotal factor for successfully producing Pd-PANI HNSs and controlling the thickness of PANI coating because both, the growth behavior of PANI and the shape preservation of Pd NCs, are highly sensitive to the acidity of the reaction solution. In addition, precise control over the amount of aniline allowed the production of Pd_{cube}-PANI HNSs with PANI coating of different thicknesses. The Pd_{cube}-PANI HNSs with a PANI coating of thickness 0.7 nm showed remarkable catalytic activity and stability for the EOR than their Pd-PANI counterparts, cubic Pd NCs, and commercial Pd/C. The XPS measurement and CO-stripping experiments exhibited that the superb performance can be attributed to modified electronic structures and high CO tolerance of Pd_{cube}-PANI HNSs by PANI coating and Pd{100} facets.

V. Reference

- 1. X. Chen, S. Shen, L. Guo and S. S. Mao, Chem. Rev., 2010, 110, 6503-6570.
- 2. S. C. Roy, O. K. Varghese, M. Paulose and C. A. Grimes, ACS Nano, 2010, 4, 1259-1278.

3. J. W. Hong, D. H. Wi, S.-U. Lee and S. W. Han, J. Am. Chem. Soc., 2016, 138, 15766-15773.

4. V. Mazumder, Y. Lee and S. Sun, Adv. Funct. Mater., 2010, 20, 1224-1231.

5. M. Shao, Q. Chang, J.-P. Dodelet and R. Chenitz, Chem. Rev., 2016, 116, 3594-3657.

6. Y.-J. Wang, N. Zhao, B. Fang, H. Li, X. T. Bi and H. Wang, Chem. Rev., 2015, 115, 3433-3467.

7. M. Liu, Z. Zhao, X. Duan and Y. Huang, Adv. Mater., 2019, 31, 1802234.

8. J. W. Hong, Y. Kim, Y. Kwon and S. W. Han, Chem. Asian J., 2016, 11, 2224-2239.

9. E. Zhu, X. Yan, S. Wang, C. Wang, M. Xu, H. Liu, J. Huang, W. Xue, J. Cai and H. Heinz, Nano Lett., 2019, 19, 3730-3736.

10. W. Ye, S. Chen, M. Ye, C. Ren, J. Ma, R. Long, C. Wang, J. Yang, L. Song and Y. Xiong, Nano Energy, 2017, 39, 532-538.

11. L. Bu, N. Zhang, S. Guo, X. Zhang, J. Li, J. Yao, T. Wu, G. Lu, J.-Y. Ma and D. Su, Science, 2016, 354, 1410-1414.

12. J. W. Hong, S. W. Kang, B.-S. Choi, D. Kim, S. B. Lee and S. W. Han, ACS nano, 2012, 6, 2410-2419.

13. F. Lu, Y. Zhang, S. Liu, D. Lu, D. Su, M. Liu, Y. Zhang, P. Liu, J. X. Wang and R. R. Adzic, J. Am. Chem. Soc., 2017, 139, 7310-7317.

14. T. Bian, H. Zhang, Y. Jiang, C. Jin, J. Wu, H. Yang and D. Yang, Nano Lett., 2015, 15, 7808-7815.

15. L. Zhang, L. T. Roling, X. Wang, M. Vara, M. Chi, J. Liu, S.-I. Choi, J. Park, J. A. Herron and Z. Xie, Science, 2015, 349, 412-416.

16. J. W. Hong, Y. Kim, D. H. Wi, S. Lee, S. U. Lee, Y. W. Lee, S. I. Choi and S. W. Han, Angew. Chem. Int. Ed., 2016, 55, 2753-2758.

17. M. Jin, H. Zhang, Z. Xie and Y. Xia, Energy Environ. Sci., 2012, 5, 6352-6357.

18. A. Chen and C. Ostrom, Chem. Rev., 2015, 115, 11999-12044.

19. H.-X. Zhang, H. Wang, Y.-S. Re and W.-B. Cai, Chem. Commun., 2012, 48, 8362-8364.

20. Y. Xie, Chem. Rec., 2019.

21. F. Li, S.-F. Zhao, L. Chen, A. Khan, D. R. MacFarlane and J. Zhang, Energy Environ. Sci., 2016, 9, 216-223.

22. M. Eswaran, R. Dhanusuraman, P.-C. Tsai and V. K. Ponnusamy, Fuel, 2019, 251, 91-97.

23. J.-X. Feng, S.-Y. Tong, Y.-X. Tong and G.-R. Li, J. Am. Chem. Soc., 2018, 140, 5118-5126.

24. K. S. Kim, H. C. Kim and J. W. Hong, Bull. Korean Chem. Soc., 2019, 40, 78-81.

25. X. Sun, N. Zhang and X. Huang, ChemCatChem, 2016, 8, 3436-3440.

26. A.-L. Wang, H. Xu, J.-X. Feng, L.-X. Ding, Y.-X. Tong and G.-R. Li, J. Am. Chem. Soc., 2013, 135, 10703-10709.

27. K. S. Kim, Y. Hong, H. C. Kim, S.-I. Choi and J. W. Hong, Chem. Eur. J., 2019, 25, 7185-7190.

28. S. Chen, Z. Wei, X. Qi, L. Dong, Y.-G. Guo, L. Wan, Z. Shao and L. Li, J. Am. Chem. Soc., 2012, 134, 13252-13255.

29. Y. Han, Z. He, S. Wang, W. Li and J. Zhang, Catal. Sci. Technol., 2015, 5, 2630-2639.

30. Z. Kalemba-Jaje, A. Drelinkiewicz, E. Lalik, E. Konyushenko and J. Stejskal, Fuel, 2014, 135, 130-145.

Z.-C. Zhang, J.-F. Hui, Z.-G. Guo, Q.-Y. Yu, B. Xu, X. Zhang, Z.-C. Liu, C.-M. Xu, J. S. Gao and X. Wang, Nanoscale, 2012, 4, 2633-2639.

32. W. Zhong, Y. Wang, Y. Yan, Y. Sun, J. Deng and W. Yang, J. Phys. Chem. B, 2007, 111, 3918-3926.

33. L. Li, L. Ferng, Y. Wei, C. Yang and H.-F. Ji, J. Colloid Interface Sci., 2012, 381, 11-16.

34. I. Sapurina and J. Stejskal, Polym. Int., 2008, 57, 1295-1325.

35. Y. Xiong and Y. Xia, Adv. Mater., 2007, 19, 3385-3391.

36. J. W. Hong, M. Kim, Y. Kim and S. W. Han, Chem. Eur. J., 2012, 18, 16626-16630.

37. F. Li, C. Yang, Q. Li, W. Cao and T. Li, Materials Letters, 2015, 145, 52-55.

38. K. Nagashree and M. Ahmed, Synthetic Metals, 2008, 158, 610-616.

39. K. Tedsree, C. W. A. Chan, S. Jones, Q. Cuan, W.-K. Li, X.-Q. Gong and S. C. E. Tsang, Science, 2011, 332, 224-228.

40. C. Bianchini and P. K. Shen, Chem. Rev., 2009, 109, 4183-4206.

41. Y. Wang, G. Wang, G. Li, B. Huang, J. Pan, Q. Liu, J. Han, L. Xiao, J. Lu and L. Zhuang, Energy Environ. Sci., 2015, 8, 177-181.

42. Q. Shi, P. Zhang, Y. Li, H. Xia, D. Wang and X. Tao, Chem. Sci., 2015, 6, 4350-4357.

43. N. Erini, S. Rudi, V. Beermann, P. Krause, R. Yang, Y. Huang and P. Strasser, ChemElectroChem, 2015, 2, 903-908.

44. X. Zhang, H. Yin, J. Wang, L. Chang, Y. Gao, W. Liu and Z. Tang, Nanoscale, 2013, 5, 8392-8397.

45. J. Wang, J. Gong, Y. Xiong, J. Yang, Y. Gao, Y. Liu, X. Lu and Z. Tang, Chem. Commun., 2011, 47, 6894-6896.

46. E. Wang, J. Xu and T. Zhao, J. Phys. Chem. C, 2010, 114, 10489-10497.