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Pt Nanoclusters Anchored on Hollow Ag-Au Nanostructures for Electrochemical Oxidation of Methanol

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Received: 10 October 2020; Accepted: 7 December 2020; Published: 9 December 2020

Abstract: The synthetic method of Pt nanocluster-anchored hollow Ag-Au nanostructures and measurements of their electrocatalytic properties for methanol oxidation reaction (MOR) are reported here. In this synthesis, uniform Ag nanospheres were prepared by reduction of silver nitrate (AgNO_3) with sodium borohydride (NaBH_4) and then hollow Ag-Au nanostructures were synthesized via galvanic replacement of the as-prepared Ag nanospheres with Au^{3+} . Finally, the reduction of potassium tetrachloroplatinate (II) (K_2PtCl_4) with ascorbic acid was performed to deposit Pt nanoclusters on the surface of hollow Ag-Au nanostructures. The hollow interior of Pt nanocluster-anchored Ag-Au nanostructures and change in the size of Pt nanoclusters by varying the injected molar ratio of Pt/Au were observed by transmission electron microscopy (TEM). Moreover, other morphological, compositional, and optical information of the obtained nanoscale materials were analyzed by X-ray diffraction analysis (XRD), inductively coupled plasma mass spectrometry (ICP-MS), and ultraviolet-visible spectroscopy (UV-vis). The electrocatalytic ability of the obtained Pt nanocluster-anchored hollow Ag-Au nanostructures toward MOR was confirmed by the results of cyclic voltametric (CV) measurements. The ease of three-step synthetic strategy and good electrocatalytic performance of the Pt nanocluster-anchored hollow Ag-Au nanostructures displayed their promising potential in the use of electrochemical oxidation of methanol.

Keywords: Pt nanoclusters; hollow Ag-Au nanostructures; galvanic replacement; methanol electrochemical oxidation

1. Introduction

Severe energy problems have attracted increasing attention recently, and direct methanol fuel cells (DMFCs) are regarded as one of the new energy resources, with their advantages of high power density, low operating temperatures, convenient transportations of methanol, etc. [1–4]. For DMFCs, platinum is the most important and frequently applied metal element for catalytic applications, and Pt-based catalyst has been a popular issue in the research realm of DMFCs. However, some factors restrict the practical and comprehensive applications of Pt-based catalysts in DMFCs. One of the factors is catalyst

poisoning effect caused by carbon monoxide (CO) which forms in the methanol oxidation reaction (MOR) as one kind of intermediate product and firmly attaches to the surface of Pt portion, leading to fewer available active sites of Pt [5–8]. Another thing that limits the extensive use of Pt-based catalysts is the extravagant price [9–11].

To overcome the two primary limits, one of the typical synthetic strategies for enhancing the electrocatalytic activity of Pt-based catalysts is combining Pt with other materials, such as dispersing Pt contents onto diverse supporters such as carbon material [12–15] and noble metallic nanoparticles, [11,16–21] or alloying Pt with other metal such as Pd [22,23], Ru [24,25], Rh [26], etc [27–32]. Recently, many advances in the synthetic approaches of Pt-based electrode materials with hollow structures have broadly demonstrated their great potential for MOR. Owing to the high surface-to-volume-ratios, elevated use of Pt, and abundant active sites, hollow structures have received much attention [33,34]. For instance, Hu and colleagues applied a galvanic replacement approach to synthesize a novel graphene-supported hollow Pt-Ni nanocatalyst, which exhibits high activity toward the MOR because of unique hollow structure and the synergistic effect between Pt and Ni [35]. More recently, Geng's team fabricated hollow Pt-Pd structures with high active surface areas, which presents a good catalytic activity and stability toward MOR [36].

Moreover, for lower usage of noble metal and a further increase of surface area, galvanic replacement is the typically used method for fabricating hollow nanostructures [37,38]. In galvanic replacement reaction, the difference of redox potential between sacrificial metallic templates, such as Ag [39–42], Co [43,44], Ni [35,45] and substitutive metal ions is the reason galvanic replacement reaction could occur spontaneously [46]. Moreover, numerous reports of galvanic replacement between Ag nanoparticles with HAuCl_4 were reported [47–49].

It is worth mentioning that designing core-shell Pt-based nanostructures is a significant way of reducing the Pt loading in fuel cell systems and ameliorating both catalytic performance and stability [50]. Therefore, research about synthesizing Au-Pt nanoscale materials with the hollow interior by galvanic replacement and their enhanced catalytic performance has been reported [39,43,51,52]. For example, Song's team fabricated hollow Au@Pt and Au@Pd core-shell nanoparticles by galvanic replacement with Ag cores and applied them in the ethanol oxidation reaction [39]. Guo and colleagues applied Co nanoparticles as sacrificial templates for synthesizing sponge-like Au-Pt core-shell nanomaterials with advantages of high efficiency and low cost [43]. Kuai and co-workers synthesized Au-Pt yolk-shell nanoparticles with ultra-high CO tolerance and enhanced catalytic activities [51]. You and colleagues synthesized Pt-on-Au hollow urchin-like nanoparticles, which present a new structure consisting of a monolayer of small Pt nano-particles (NPs) uniformly overgrown on an Au hollow nanourchin [52]. More recently, Tan and co-workers successfully fabricated hollow Au@Pt NPs with favorable electrochemical performance using a seeded-growth method. This core-shell structure helps to prevent agglomeration, and can better maintain long-term stability to MOR by effectively removing intermediates [53].

Here, we report an easy and low-cost method for synthesizing Pt nanocluster-anchored hollow Ag-Au nanostructures. The final nanostructures can be gained by a three-step successive process: (1) synthesis of uniform Ag nanospheres by reduction of AgNO_3 , (2) preparation of hollow Ag-Au nanostructures by galvanic replacement of the as-prepared Ag nanospheres with Au^{3+} , and (3) deposition of Pt nanoclusters on hollow Ag-Au nanostructures by reduction of K_2PtCl_4 with ascorbic acid. The morphological, optical, crystallographic, compositional, and electrocatalytic information of resultant products were measured and collected by transmission electron microscopy (TEM), ultraviolet-visible spectroscopy (UV-vis), X-ray diffraction analysis (XRD), inductively coupled plasma mass spectrometry (ICP-MS), and cyclic voltametric (CV) measurements. The synthetic strategy applied in this report is simple and can be extended for preparing more complex bimetallic or multimetallic nanostructures. In addition, the good electrochemical catalytic performance of the nanostructures reveals the possibility of their application in DMFCs.

2. Results and Discussion

2.1. Physical and Chemical Characterizations

Scheme 1 displays a general synthetic approach to fabricating Pt nanocluster-anchored hollow Ag-Au nanostructures. As illustrated, the whole procedure begins with the synthesis of uniform Ag nanospheres. The prepared Ag nanospheres are used as the sacrificial template in the preparation of hollow Ag-Au nanostructures. Finally, Pt nanoclusters are generated on the surface of hollow Ag-Au nanostructures by reducing K_2PtCl_4 with L (+)—ascorbic acid in an aqueous solution containing (cetyltrimethylammonium bromide) CTAB.

Scheme 1. Schematic illustration of a successive procedure for preparing Pt nanocluster-anchored hollow Ag-Au nanostructures: (a) starting synthesis of uniform Ag nanospheres by adding $NaBH_4$ solution into the mixed aqueous solution of $AgNO_3$, EDTA and Pluronic P123, (b) transforming Ag nanospheres into hollow Ag-Au nanostructures by injecting $HAuCl_4$ solution and (c) coating Pt nanoclusters on the surface of hollow Ag-Au nanostructures.

It should be noted that Pluronic P123 [54,55] was used as a capping agent to stabilize Ag nanocrystals which appear at an early stage in the synthesis of Ag nanospheres. In addition, EDTA was used for slowing down the reduction speed of $AgNO_3$ because it possesses hexadentate ligand and chelate function group which can form a complex with Ag^+ [56]. Accordingly, Ag nanospheres with narrow size distribution and good stability were successfully prepared. Figure 1a,b displays typical TEM images of the as-prepared Ag nanospheres with an average diameter of 7.4 ± 1.2 nm (Figure S1a).

Figure 1. TEM image (a) and HR-TEM image (b) of Ag nanospheres and (c) digital photograph of the resultant solution of Ag nanospheres.

Afterwards, the transformation of Ag nanospheres into hollow Ag-Au nanostructures was achieved by galvanic replacement with gold ions. Referring to the involved reaction mechanism, $[\text{AuCl}_4]^-$ ions were supposed to adjoin to the surface of Ag nanospheres, then the exchange of electrons happened immediately. With the reaction went on, Ag was replaced by Au from surface to interior of Ag nanospheres [40,49,57,58]. Based on the mechanism, proper reaction kinetics would be a critical factor in the formation of hollow Ag-Au nanostructures. Thus, continuous and slow injection of the HAuCl_4 solution by syringe pump was adopted to ensure appropriate reaction speed, Ag has time to completely dissolve from certain sites, leaving Au particles on the Au surface, forming a hollow Ag-Au nanostructure [59]. The hollow interior of the obtained Ag-Au nanostructures with an average diameter of 11.4 ± 1.4 nm could be observed through TEM measurements (Figure 2a,b) and size distribution analysis.

Figure 2. TEM image (a) and HR-TEM image (b) of hollow Ag-Au nanostructures and (c) digital photograph of resultant solution of hollow Ag-Au nanostructures.

Finally, deposition of Pt on hollow Ag-Au nanostructures was made by reduction of K_2PtCl_4 with L (+)—ascorbic acid in an aqueous solution of CTAB. The injected molar ratio of Pt/Au in our study was set from 1 to 3. Figure 3a–c shows TEM images of the Pt nanocluster-anchored Ag-Au hollow nanostructures at different molar ratios of Pt/Au. As HR-TEM images shown in Figure 3d–f, the obtained nanostructures exhibited rough surface due to sporadic Pt deposition on the surface of hollow Ag-Au nanostructures. With the injected Pt/Au molar ratio increasing, the average diameter of final products displayed narrow size distribution and varied from 10.4 ± 0.9 nm to 12.4 ± 1.4 nm. We can observe the enlargement of the particle size and the surface roughness under the same magnification. When the surface changes from flat to very wrinkled, the surface area and exposure of edge atom also increases, which can bring many benefits to the catalytic activity. Moreover, the HAADF-STEM images (Figure 3g–i) of the nanostructures showed the relative position of the elements, namely the bright portion suggests a high portion of the elements and vice versa. In detail, the lightness of the

bright portion in Figure 3i is higher than that in Figure 3g,h, meaning more concentrated Pt element is anchored on the sample showed in Figure 3i. On the other hand, an obvious contrast between the bright and dark portion in Figure 3g–i proved that hollow structure is uniformly synthesized. Therefore, the hollow interiors of the as-obtained nanostructures could be observed clearly.

Figure 3. TEM images (a–c), HR-TEM images (d–f), and HAADF-STEM images (g–i) of Pt nanocluster-anchored hollow Ag-Au nanostructures with an injected molar ratio of Pt/Au from 1 to 3. The inset pictures in HR-TEM images are digital photographs of resultant solution of the obtained nanostructures.

Then, compositional information of all the as-prepared Pt nanocluster-anchored hollow Ag-Au nanostructures was collected by ICP-MS analysis (Table 1). From Table 1, when comparing the actual amount of Pt to theoretical counterpart, considerable Pt loss in the products could be observed obviously, which range from 39.47% to 46.24%. The analysis result also confirmed existence of unreplaced Ag content in the resultant nanostructures, which indicating the incomplete galvanic replacement of Ag nanospheres. Additionally, as for the Pt/Au molar ratio of our products, the results were linearly dependent to the value of the injected molar ratio (Figure 4), which were calculated as 0.87, 1.74 and 2.26. Moreover, energy-dispersive X-ray (EDX) analysis was performed for further understanding of component information of the nanostructures (Figures S2–S4).

Figure 4. Plots of the Pt/Au molar ratio of Pt nanocluster-anchored hollow Ag-Au nanostructures at actual value (black line) and theoretical value (red line) against the injected Pt/Au molar ratio.

Table 1. Compositional information of Pt nanocluster-anchored hollow Ag-Au nanostructures with injected molar ratios of Pt/Au from 1 to 3 confirmed by ICP-MS.

	Sample 1	Sample 2	Sample 3
Ag/ppb (%)	1376.3 (13.68)	1598.9 (11.42)	1769.0 (10.26)
Au/ppb (%)	4666.9 (46.40)	4569.9 (32.62)	4782.5 (27.73)
Pt/ppb (%)	4015.0 (39.92)	7839.9 (55.96)	10,696.4 (62.01)
Molar ratio (Pt/Au)	0.87	1.74	2.26
Theoretical Pt mass/ μ g	66.33	132.66	198.98
Actual Pt mass/ μ g	40.15	78.40	106.96
Pt loss (%)	39.47	40.90	46.24

Afterwards, the UV-vis spectra (Figure 5) of Ag nanospheres, Ag-Au nanostructures, and Pt nanocluster-anchored hollow Ag-Au nanostructures were collected. A narrow absorption peak at 397 nm caused by the surface plasmon resonance of Ag nanospheres could be observed in Figure 5. As for hollow Ag-Au nanostructures, the spectra display relatively broader absorption peak than that of Ag nanospheres at a wavelength of about 427 nm. In the case of Pt nanocluster-anchored hollow Ag-Au nanostructures, the suppression and disappearance of the absorption peak at the wavelength that could initially be observed from Au-Ag nanostructures as the molar ratio of Pt/Au increased, since the deposition of Pt on the surface of Ag-Au nanostructures. Specifically, a red shift of absorption peak happened when the molar ratio of Pt/Au equals 1 and further suppression of the absorption peak could be seen obviously for the nanocomposite with Pt/Au molar ratio of 2. When the molar ratio of Pt/Au reaches 3, a more stable Pt shell has been fabricated, the absorption peak vanished and be substituted by a downslope absorption curve [60].

Figure 5. Normalized UV-vis spectra of Ag nanospheres (black line), hollow Ag-Au nanostructures (red line), and Pt nanocluster-anchored hollow Ag-Au nanostructures with injected molar ratios of Pt/Au at 1 (blue line), 2 (purple line) and 3 (green line).

XRD patterns of the Pt nanocluster-anchored hollow Ag-Au nanostructures with different Pt/Au molar ratio are displayed in Figure 6. When compared to standard diffraction patterns of Ag (JCPDS 65-2871), Au (JCPDS 65-2870) and Pt (JCPDS 65-2868), the overlap of diffraction peaks could be observed from that they are in the range of JCPDS standard diffraction cards. In addition, the diffraction peaks located at 2 theta angles range of $38.24\text{--}38.68^\circ$, $44.64\text{--}45.62^\circ$, $65.32\text{--}66.44^\circ$ and $78.90\text{--}79.56^\circ$ are corresponding to (111), (200), (220), and (311) planes of face-centered-cubic (FCC) structure, respectively, which implying alloy structures of the products with different Pt/Au molar ratios, in spite low intensity of diffraction peaks of samples.

Figure 6. XRD patterns of Pt nanocluster-anchored hollow Ag-Au nanostructures with injected molar ratios of Pt/Au at 1 (black line), 2 (red line) and 3 (blue line).

2.2. Electrocatalytic Characterization

CV measurements of the Pt nanocluster-anchored hollow Ag-Au nanostructures with a different injected molar ratio of Pt/Au (1 to 3) and commercial 40% Pt/C catalysts were performed in N_2 -saturated $0.5\text{ M H}_2\text{SO}_4 + 1.0\text{ M CH}_3\text{OH}$ solution at room temperature. The CV results were displayed in Figure 7a and the current was normalized by the Pt loading. From Figure 7a, forward and backward current peaks, which correspond to the oxidation of methanol and formation of intermediate products respectively [19], can be observed clearly in CV curves of all catalysts so that confirming their electrocatalytic activity for MOR. Therefore, the current intensity of forward sweep in CV curves of MOR could be assumed as an indicator of the magnitude of electrocatalytic properties of catalysts [11]. Specifically, in the case of the Pt nanocluster-anchored hollow Ag-Au nanostructures with a different molar ratio of Pt/Au, the CV curves displayed higher mass activity with the amount of Pt loading increased to a certain level. When the molar ratio of Pt/Au are 1 and 2, the mass activity of correspondents reached $57.2\text{ mA}\cdot\text{mg}^{-1}$ and $86.5\text{ mA}\cdot\text{mg}^{-1}$, respectively. As for the Pt nanocluster-anchored hollow Ag-Au nanostructures with a molar ratio of Pt/Au equals 3, the mass activity soared to $323.1\text{ mA}\cdot\text{mg}^{-1}$. Additionally, commercial 40% Pt/C catalyst was used for the sake of comparison in our study and it displayed a mass activity reached up to $259.3\text{ mA}\cdot\text{mg}^{-1}$, which was lower than that of the hollow nanostructure at Pt/Au molar ratio of 3. However, when further increase the thickness of Pt layer on Ag-Au core by lifting the Pt/Au molar ratio to 4 (identified as Sample 4), the activity of which has greatly decreased, as shown in Figure S5. Furthermore, the small size of the as-synthesized uniformly crystallized nanostructures is believed to offers greater surface area and more exposure of catalytic sites of Pt, which accelerates the MOR process [33,61]. This phenomenon was reasonable: Owing to the high surface-to-volume-ratios, elevated use of Pt and abundant active sites, our catalyst exhibits high activity toward the MOR. Taken together, better durability with thicker layer could be attributed to more generation of Pt stable phase toward MOR [62–64]. The results also displayed the immense potential of as-prepared Pt nanocluster-anchored hollow Ag-Au nanostructures as efficient Pt-based catalysts in applications of DMFCs. The long-term stability of the Pt nanocluster-anchored hollow Ag-Au nanostructures (injected molar ratio of Pt/Au, 3:1) and commercial 40% Pt/C catalysts was evaluated by chronoamperometric measurement under a constant potential of 0.70 V for 5000 s as shown in Figure 7b, which is used to determine the effect of carbon monoxide adsorption during methanol oxidation. Pt nanocluster-anchored hollow Ag-Au nanostructures produced an initial specific activity of $193.3\text{ mA}\cdot\text{mg}^{-1}$ and a final specific activity of $79.2\text{ mA}\cdot\text{mg}^{-1}$, corresponding to 40.97% of the initial response. Commercial 40% Pt/C produced an initial specific activity of $153.9\text{ mA}\cdot\text{mg}^{-1}$ and a final specific activity of $62.4\text{ mA}\cdot\text{mg}^{-1}$, corresponding to 40.54% of the initial response. The polarization currents decrease rapidly at the initial stage, which is due to the formation of intermediate species during MOR [65,66]. In this manner, Pt nanocluster-anchored hollow Ag-Au nanostructures maintained a specific activity 0.43% greater than commercial 40% Pt/C for the oxidation of methanol during chronoamperometry, which further reveals the high electrochemical durability of the as-prepared nanostructure.

For a more comprehensively understanding of the electrocatalytic performance, CV measurement of the Pt nanocluster-anchored hollow Ag-Au nanostructures with a different injected molar ratio of Pt/Au (1 to 3) were evaluated. Commercial 40% Pt/C catalyst was selected as a reference catalyst. CV curves were performed in N_2 -saturated $0.5\text{ M H}_2\text{SO}_4$ solution at room temperature (Figure 8a). The electrochemical active surface areas (ECSA) of the as-prepared hollow nanostructure and the commercial catalyst were calculated to be 9.85 (Sample 1), 10.42 (Sample 2), 19.32 (Sample 3) and $18.02\text{ (40\% Pt/C) m}^2\cdot\text{g}^{-1}$, respectively (Table S1) by hydrogen desorption peak zone between -0.2 to 0.2 V vs. Ag/AgCl electrode. Additionally, several indicators of catalytic performance, including Pt loading, specific activity, mass activity, ECSA, and peak potential of testing samples, were listed in Figure 8b and Table S1. Uniform products with hollow nanostructures may be responsible for (electrochemical surface area) ESCA value and offer many active sites, indicating the better electrocatalytic performance.

Figure 7. (a) CV curves of Pt nanocluster-anchored hollow Ag-Au nanostructures with injected molar ratios of Pt/Au at 1 (black line), 2 (red line) 3 (blue line) and commercialized 40% Pt/C catalysts (purple line) recorded in N₂-saturated 1 M CH₃OH + 0.5 M H₂SO₄ solution. (b) Chronoamperometric curves of Pt/Au at 3 (blue line) and commercialized 40% Pt/C catalysts (purple line) recorded at 0.70 V (vs. Ag/AgCl) in N₂-saturated 1 M CH₃OH + 0.5 M H₂SO₄ solution.

Figure 8. (a) CV curves of Pt nanocluster-anchored hollow Ag-Au nanostructures with injected molar ratios of Pt/Au at 3 (black line) and commercialized 40% Pt/C catalysts (red line) recorded in N₂-saturated 0.5 M H₂SO₄ solution. (b) Electrochemical performance of Pt nanocluster-anchored hollow Ag-Au nanostructures with injected molar ratios of Pt/Au at 1 (black line), 2 (red line) 3 (blue line) and commercialized 40% Pt/C catalysts (purple line) recorded in N₂-saturated 1 M CH₃OH + 0.5 M H₂SO₄ solution.

However, when compared to the theoretical amount of Pt from the testing result of ICP-MS analysis, it could be observed that a considerable amount of Pt loss occurred during centrifugation processes for washing the resultant products (Table S2). Moreover, due to the strong attachment of CTAB onto the surface of the Pt nanocluster-anchored hollow Ag-Au nanostructures and the electrocatalytic activity intensively relies on the accessibility of catalysts to the electrolyte, it could be inferred that the appropriate extent of centrifugation, neither be inadequate for removing CTAB nor so excessive that leading to aggregation of nanocomposites, was another key factor which influences the catalytic performance of the obtained catalysts for MOR. Therefore, further exploration of efficient and proper washing method with lower Pt loss would be needed for practical application of Pt-anchored hollow Ag-Au nanostructures in MOR and DMFCs.

3. Materials and Methods

3.1. Materials

AgNO_3 , NaBH_4 , sulfuric acid (H_2SO_4), methanol (CH_3OH) were purchased from Samchun Pure Chemical Corp. Nafion perfluorinated resin solution (5 wt.% in lower aliphatic alcohols and water, contains 15–20% water), K_2PtCl_4 , gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), L (+)—ascorbic acid, ethylenediaminetetraacetic acid (EDTA) and hexadecyltrimethylammonium bromide (CTAB) were purchased from Sigma-Aldrich Chemical Corp. Pluronic P123 (Poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol)) was purchased from BASF Corp. Commercial 40% Pt/C catalyst (y are located in the range of JCPDS standard diffraction cards. In addition, the diffraction peaks located at 2 theta angles range of $38.24\text{--}38.68^\circ$, $44.64\text{--}45.62^\circ$, $65.32\text{--}66.44^\circ$ and $78.90\text{--}79.56^\circ$ are corresponding to (111), (200), (220), and (311) planes of FCC structure, respectively, which implying alloy structures of the products with different Pt/Au molar ratios, in spite low intensity of diffraction peaks of samples.

3.2. Synthesis of Uniform Ag Nanospheres

Synthesis of uniform Ag nanospheres could be described as follows. A mixture of 0.1 mL of 0.1 M AgNO_3 solution with 0.1 mL of 1 M EDTA solution was added into 9 mL of 0.2 g Pluronic P123 homogeneous aqueous solution, then the blended solution was stirred for 0.5 h at room temperature. Afterwards, 0.6 mL of 0.3 M freshly made ice-cold NaBH_4 solution was added into the mixed solution quickly to initiate the reaction and vigorous stirring was sustained for daylong time to complete the synthesis of Ag nanospheres. After the addition of NaBH_4 solution, immediate color change of the solution, from transparent into blackish green and light yellow eventually, could be observed.

3.3. Synthesis of Hollow Ag-Au Nanostructures

In the synthesis of hollow Ag-Au nanostructures via galvanic replacement, the as-prepared Ag nanospheres were served as sacrificial materials to react with HAuCl_4 . Specifically, 2 mL of 3.4×10^{-4} M HAuCl_4 solution was injected into 2 mL of Ag nanosphere solution by a syringe pump at an injection rate of 1 mL/h with vigorous stirring for 6 h. With continuous injection went on, the color of the solution was changed from light yellow to orange-yellow eventually.

3.4. Synthesis of Pt Nanocluster-Anchored Hollow Ag-Au Nanostructures

Coating of Pt nanoclusters on hollow Ag-Au nanostructures was attained by reduction of K_2PtCl_4 with L (+)—ascorbic acid. Specifically, three same samples of each containing 2 mL of hollow Ag-Au nanostructures solution and 2 mL of 0.1 M CTAB solution were prepared first. Then, 34, 68 and 102 μL of 0.01 M newly prepared K_2PtCl_4 solutions [67,68] were added to the above-mentioned samples, at Pt/Au molar ratio which range from 1 to 3. The three samples were labeled as Sample 1, Sample 2, and Sample 3, respectively, and they were left undisturbed for 0.5 h to complete complexation of CTAB with $[\text{PtCl}_4]^{2-}$. Finally, the addition of 68, 136 and 204 μL of 0.1 M L (+)—ascorbic acid solution to each sample was followed with vigorous stirring for 36 h to complete the reaction. The resultant solution which displayed color of dark brown was centrifuged for 3 times (12,000 rpm, 30 min) and the precipitate was redispersed in 0.5 mL DI water for further characterizations (TEM and ICP-MS).

3.5. Physical and Chemical Characterizations

TEM and HR-TEM images were obtained from JEOL JEM-2100F transmission electron microscope equipped with EDX spectroscopy detector and Cs corrector at accelerating voltage of 200 kV. UV-vis spectrum was collected from Perkin-Elmer Lambda 35 UV-vis spectrometer. Information on chemical composition was characterized by Perkin-Elmer SCIEX NexION 350D ICP-mass spectrometer.

XRD patterns were obtained with a Bruker D8 DISCOVER high-resolution X-ray diffractometer (with Cu K α radiation, $\lambda = 1.542 \text{ \AA}$).

3.6. Electrocatalytic Characterization

CV measurements were performed with a CH instrument 660E electrochemical workstation with three electrodes systems at room temperature. Glassy carbon electrode with 3.0 mm diameter was used as working electrode. Ag/AgCl electrode and Pt net were selected as a reference and counter electrodes, respectively. In CV measurements, 3 μL sample solution was dripped onto the surface of glassy carbon electrode and was dried under an infrared lamp for 10 min. A mixture solution containing 1.0 M CH₃OH and 0.5 M H₂SO₄ was bubbled with N₂ gas for 15 min before the measurements. The whole process was conducted under the protection of N₂ gas and in a potential range of 0 to 1.0 V (vs. Ag/AgCl) at sweep rate of 0.05 V/s. The MOR stability test was performed in N₂-saturated 1 M CH₃OH + 0.5 M H₂SO₄ solution by chronoamperometry at 0.70 V (vs. Ag/AgCl).

4. Conclusions

In conclusion, Pt nanocluster-anchored hollow Ag-Au nanostructures were synthesized by involving reduction reaction of metal ions (Ag⁺, Pt²⁺) and galvanic replacement reaction in aqueous solution (Ag with Au³⁺). Under optimized conditions, uniform and stable products with hollow nanostructures could be prepared reproducibly. It should be pointed out that involvement of crucial chemicals (Pluronic P123, EDTA, and CTAB) during the synthesis and controlling injection rate of Au stock solution by syringe pump were critical parameters for ensuring stability and uniformity. Owing to the high surface-to-volume-ratios, elevated use of Pt and abundant active sites, hollow structures present a favorable catalytic activity and stability toward MOR. The results of electrochemical measurements showed a higher mass activity and ECSA of the nanostructures than commercial 40% Pt/C catalyst, which indicated the better electrocatalytic performance of them. The experimental results also showed the immense potential of the nanostructures as Pt-based catalysts in the further application for DMFCs. We believe this work may inspire many researchers who work on optimizing and inventing a new type of catalyst with magnificent structures using noble metals. Also, this study can be further extended into other applications such as hydrogen evolution reaction (HER). Moreover, the synthetic approach applied in this study offered a simple and economical way for producing many kinds of complex nanoarchitectures which could find novel applications in various areas.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/10/12/1440/s1>, Figure S1: Size distribution of (a) Ag nanospheres, (b) hollow Ag-Au nanostructures, and (c) Pt nanocluster-anchored hollow Ag-Au nanostructures with injected molar ratio of Pt/Au at 3, Figure S2: EDX spectrum (left) and compositional information (right) of Pt nanocluster-anchored hollow Ag-Au nanostructures with injected molar ratio of Pt/Au at 1, Figure S3: EDX spectrum (left) and compositional information (right) of Pt nanocluster-anchored hollow Ag-Au nanostructures with injected molar ratio of Pt/Au at 2, Figure S4: EDX spectrum (left) and compositional information (right) of Pt nanocluster-anchored hollow Ag-Au nanostructures with injected molar ratio of Pt/Au at 3, Figure S5: CV curves of Pt nanocluster-anchored hollow Ag-Au nanostructures with injected molar ratios of Pt/Au at 3 (blue line) and 4 (yellow line) recorded in N₂-saturated 1 M CH₃OH + 0.5 M H₂SO₄ solution. Table S1: Results of electrochemical measurements of our samples and commercial catalyst for electrochemical oxidation of methanol, Table S2: Pt amount in loading solutions of the nanostructures and commercial catalyst in CV measurements confirmed by ICP-MS.

Author Contributions: Conceptualization, Y.P. and X.L.; methodology, Y.P. and W.Z.; formal analysis, X.L. and X.Q.; investigation, X.L.; data curation, X.L. and X.Q.; writing—original draft preparation, X.L.; writing-review and editing, X.Q., B.Y., and H.H.; supervision, Y.P.; project administration, Y.P.; funding acquisition, Y.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (NRF-2018R1D1A1B07051249), Nano Material Technology Development Program (NRF-2015M3A7B6027970) and Science and Technology Amicable Relationships (STAR) Program (NRF-2019K1A3A1A21031052) of MSIT/NRF.

Conflicts of Interest: The authors declare no conflict of interest.

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