

Article

Hydrothermal Method Using DMF as a Reducing Agent for the Fabrication of PdAg Nanochain Catalysts towards Ethanol Electrooxidation

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Abstract: In this article, we developed a facile one-step hydrothermal method using dimethyl formamide (DMF) as a reducing agent for the fabrication of PdAg catalyst. The scanning electron microscope (SEM) and transmission electron microscopy (TEM) images have shown that the as-synthesized PdAg catalyst had a nanochain structure. The energy-dispersive X-ray analyzer (EDX) spectrum presented the actual molar ratio of Pd and Ag in the PdAg alloy. Traditional electrochemical measurements, such as cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS), were performed using a CHI 760D electrochemical analyzer to characterize the electrochemical properties of the as-synthesized catalyst. The results have shown that the PdAg catalyst with a nanochain structure displays higher catalytic activity and stability than pure Pd and commercial Pd/C catalysts.

Keywords: hydrothermal; PdAg; nanochain; ethanol oxidation

1. Introduction

Nowadays, direct ethanol fuel cells (DEFCs) as a promising clean energy have attracted great interest for their low cost and toxicity [1,2]. Moreover, DEFCs act as a power source because of their high energy density and low emissions, and they can be produced in a sustainable way [3]. However, there are still some limitations to realize the commercialization of DEFC, for example the high cost of catalysts, and the poor activity and stability of catalysts. To solve these problems, nanostructure electrocatalysts have been well designed to improve the catalytic activity and durability for ethanol electrooxidation [4–6].

As is known, Pt and Pt-based catalysts, such as PtSn [7], PtAu [8] and PtNi [9], with high activity have been widely investigated by researchers for ethanol electrooxidation in the past few decades. However, the high price and limited resources of Pt may hinder the application of Pt in the field of fuel cells. Pd is an active material for ethanol electrooxidation in alkaline media, which is less expensive and more active than Pt and Pt-based catalysts [10–12]. Thus, Pd and Pd-based catalysts have attracted much attention as effective anode catalysts for DEFCs. According to previous studies, it has been found that the particle size, shape, and surface compositions of the catalysts have great impact on the catalytic properties of the catalysts [13,14]. To enhance the catalytic activity and reduce the cost, another transition metal can be introduced into the Pd catalyst. In addition, to effectively obtain Pd-based catalysts with large surface areas and abundant active sites, it is important to manipulate the morphology and size of the as-prepared catalysts. Up to now, lots of methods have been attempted to achieve Pd-based catalysts with various kinds of shapes and sizes, for example nanocube PdAu

catalysts [15], porous PdPt catalysts [16], and core shell structure PdCu catalysts [17], which have been employed in the field of DEFCs. Pd combined with another transition metal can modify the electronic structure of the Pd catalyst and reduce the experimental cost [18,19]. However, PdAg catalysts for ethanol oxidation in alkaline media with a nanochain structure are rarely reported, and the addition of Ag can not only reduce the cost of the experiment, but can also enhance the catalytic activity and durability of Pd catalysts.

In this article, we synthesized nanochain-structure PdAg catalysts via a one-step hydrothermal method, using dimethyl formamide (DMF) as a reducing agent. The as-prepared nanochain PdAg catalysts can significantly promote the catalytic activity towards the ethanol oxidation reaction in alkaline media. For comparison, the activity and stability of commercial Pd/C towards ethanol electrooxidation was also studied by cyclic voltammetry (CV) and chronoamperometry (CA) measurements. The structure, morphologies and compositions of the as-synthesized catalysts were characterized by SEM, TEM, and XRD.

2. Results and Discussion

The morphology of the as-synthesized PdAg catalyst was characterized by SEM. As shown in Figure 1, nanochain-structure PdAg catalysts were synthesized by the hydrothermal method using DMF as a reducing agent. It can be seen that the nanochain-structure PdAg was constituted by many irregular nanoparticles. The small-size irregular nanoparticles may increase the catalytic active surface of the as-synthesized catalyst, which may further enhance the catalytic activity of the catalyst for ethanol oxidation in alkaline media. Furthermore, EDX analysis was also carried out to detect the chemical composition of the as-synthesized PdAg catalyst, which was shown in Figure 1B. Apparently, the peak of the Si element corresponded to the substrate. The EDX spectrum data confirms that the molar ratio between Pd and Ag is close to 1.1:1, which is nearly consistent with the rate of charge.

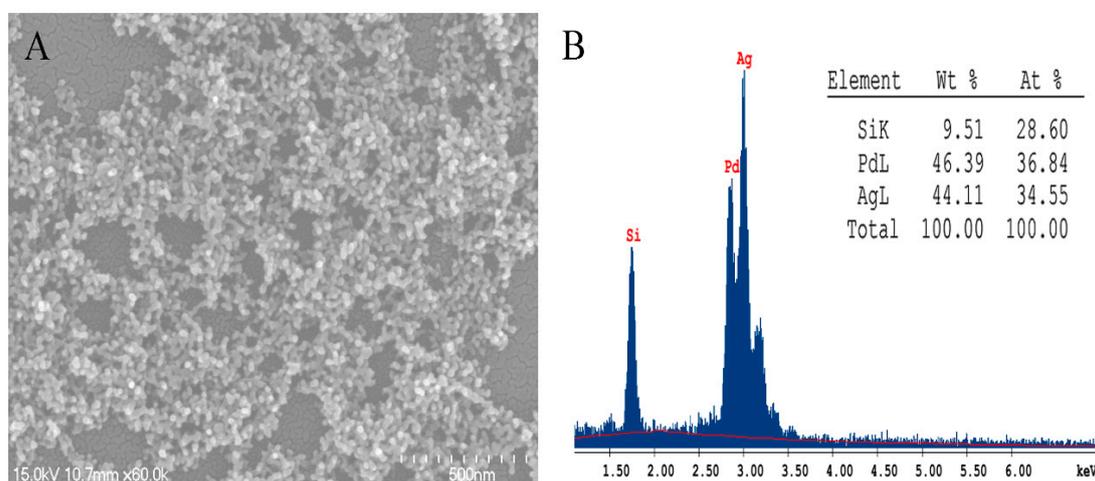


Figure 1. SEM (scanning electron microscope) image of PdAg catalyst (A); EDX (energy-dispersive X-ray analyzer) spectrum of PdAg catalyst (B).

In order to further analyze the structure and morphology of the PdAg catalyst, TEM images with different magnifications were displayed in Figure 2. As known, the DMF organic solvent is a powerful reducing agent to reduce Ag^+ . The reaction mechanism is as the following equation [20]: $\text{HCONMe}_2 + 2\text{Ag}^+ + \text{H}_2\text{O} \rightarrow 2\text{Ag} + \text{Me}_2\text{NCOOH} + 2\text{H}^+$. Ag is more active than Pd, so it is easy for DMF solution to reduce Pd^{2+} to Pd^0 nanoparticles. The presence of the Br^- ions enables us to etch the as-synthesized nanoparticles to form the irregular nanoparticles [21]. The introduction of (polyvinylpyrrolidone) PVP in this experiment is to prevent the irregular particles from agglomerating together, because the as-synthesized PdAg particles can coordinate with N or O elements in PVP,

which can generate a covered layer on the surface of the PdAg catalyst [22]. In addition, protonated carbonyl groups provided PVP with abundant positive charges, and the electrostatic repulsion effect can disperse the as-synthesized irregular PdAg particles. The PVP polymer chains connected to each other easily to form the nanochain-structure PdAg catalyst [23].

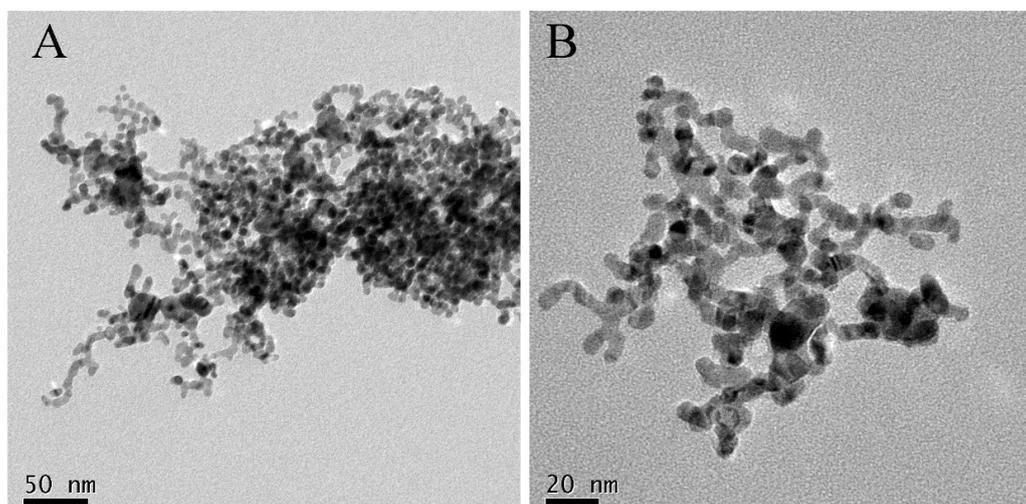


Figure 2. TEM images of the as-synthesized PdAg catalysts with different magnifications.

The structural features of the as-synthesized PdAg and Pd catalysts were characterized by XRD, and the XRD profiles are presented in Figure 3. Four typical diffraction peaks at around 39.4° , 45.9° , 67.1° and 81.3° , corresponding to the (111), (200), (220), and (311) lattice planes of Pd, can be evidently observed in Figure 3 [24,25]. It is worth noticing that there are some slight shifts of diffraction peaks on the PdAg catalyst compared to the pure Pd catalyst. This phenomenon suggests that the addition of Ag can cause the lattice contraction of the Pd catalyst and the formation of the PdAg alloys [26]. Moreover, the diffraction peaks of Ag or Ag oxides cannot be observed, which can further confirm that the PdAg alloys are synthesized.

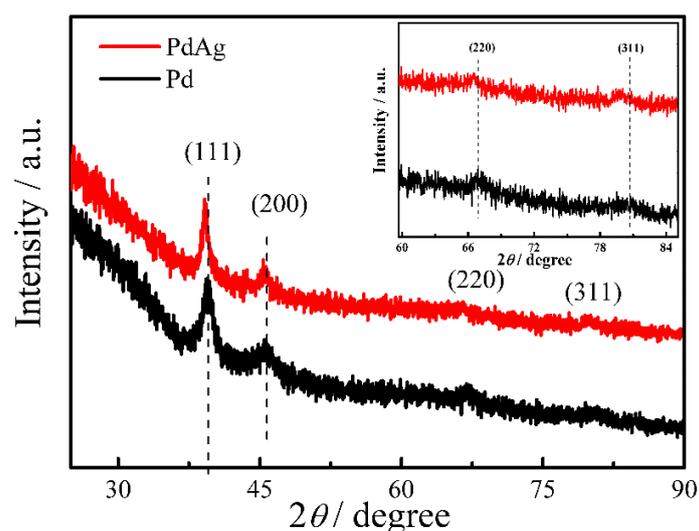


Figure 3. XRD (X-ray diffraction) patterns of as-synthesized PdAg and Pd catalysts.

CV curves of the as-prepared PdAg, Pd and commercial Pd/C catalysts, shown in Figure 4A, were obtained using cyclic voltammetry measurement in 1.0 M KOH from -0.8 to 0.3 V. It can be

observed in Figure 4A that the typical cathodic peaks of the as-synthesized catalysts at around -0.4 V are related to the reduction of Pd oxide [27]. The reduction peak of the PdAg catalyst was higher and shifted to negative potential compared with the pure Pd and commercial Pd/C catalysts, which may be ascribed to the simultaneous reduction of PdO and Ag oxides. The electrochemical surface area (ECSA) is usually applied to assess the electrochemical active sites of the catalysts, which can be deduced to be $402.1 \text{ cm}^2 \cdot \text{mg}^{-1}$, $328.2 \text{ cm}^2 \cdot \text{mg}^{-1}$ and $241.8 \text{ cm}^2 \cdot \text{mg}^{-1}$ according to the following Equation (1) [27,28]:

$$ECSA = \frac{Q}{0.43 \times [Pd]} \quad (1)$$

The value $0.43 \text{ (mC} \cdot \text{cm}^{-2})$ is a constant charge value assumed for the reduction of Pd oxide on the surface of the catalysts; Q in mC can be calculated according to the integration of the area under the reduction peak of the CVs in Figure 4A; $[Pd]$ in mg represents the mass of Pd loading on the surface of the (glassy carbon electrode) GCE. The results of the ECSA are shown in Table 1. It can be found that the ECSA of the as-synthesized PdAg catalyst is remarkably higher among all these catalysts, which indicates that the addition of Ag can enhance the electrochemical active area of the Pd catalyst.

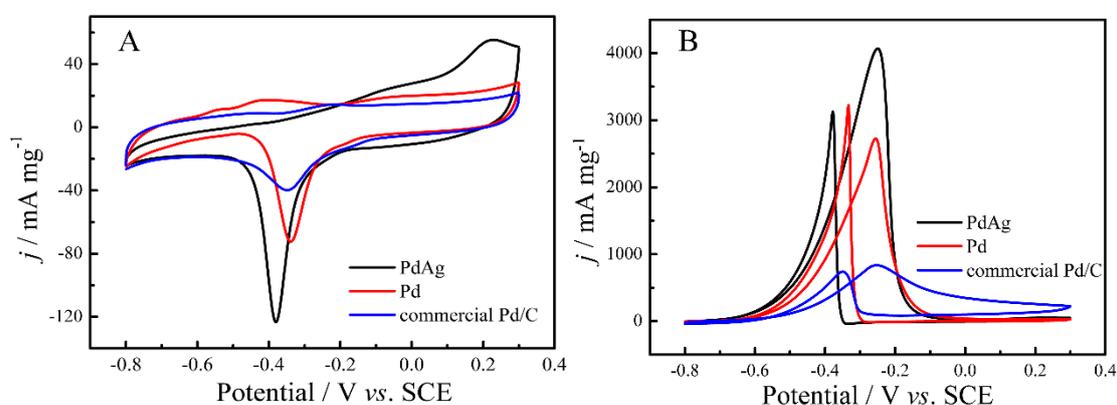


Figure 4. Cyclic voltammograms of the as-prepared PdAg, Pd and commercial Pd/C in (A) 1.0 M KOH; (B) 1.0 M $\text{C}_2\text{H}_5\text{OH}$ + 1.0 M KOH solution, at a scan rate of $50 \text{ mV} \cdot \text{s}^{-1}$.

Table 1. Comparison of properties among the as-prepared catalysts.

Catalysts	ECSA (Electrochemical Surface Area) ($\text{cm}^2 \cdot \text{mg}^{-1}$)	I_f ($\text{mA} \cdot \text{mg}^{-1}$)	I_b ($\text{mA} \cdot \text{mg}^{-1}$)	I_f/I_b
PdAg	402.1	4098.2	3137.7	1.3
Pd	328.2	2735.3	3207.8	0.9
Commercial Pd/C	241.8	827.2	756.9	1.1

The electrochemical catalytic activity of all these catalysts toward ethanol oxidation in alkaline media was further investigated by testing the catalysts in 1.0 M $\text{C}_2\text{H}_5\text{OH}$ and 1.0 M KOH solution. The mass normalization activity was usually used to evaluate the electrocatalytic activity of the as-prepared catalysts. In Figure 4B, the forward anodic peak current density of the PdAg catalyst is about $4098.2 \text{ mA} \cdot \text{mg}^{-1}$, which is higher than the pure Pd catalyst ($2735.3 \text{ mA} \cdot \text{mg}^{-1}$) and commercial Pd/C catalyst ($827.2 \text{ mA} \cdot \text{mg}^{-1}$). This result may suggest that the introduction of Ag to the Pd catalyst promotes the activity of the Pd catalyst. Moreover, the ratio of the forward peak current density to the backward peak current density (I_f/I_b) can be calculated to evaluate the tolerance of the catalysts to the poison species on the surface of the as-prepared working electrodes [29–31]. As seen in Table 1, the I_f/I_b value of the PdAg catalyst is about 1.3, higher than the pure Pd (0.9) and commercial Pd/C (1.1) catalyst. This result indicates that the addition of Ag to the Pd can enhance the poison tolerance of the Pd catalyst.

To further investigate the stability of the as-prepared catalysts, the chronoamperometric measurement was carried out in 1.0 M KOH + 1.0 M C₂H₅OH solution at −0.3 V. As can be learned from Figure 5, the current density of the as-prepared PdAg and pure Pd catalysts decayed rapidly in the initial period and gradually remained stable, which is ascribed to the formation of intermediate carbonaceous species (such as CO_{ads}) on the surface of catalysts during ethanol electrooxidation [32]. After 3600 s, the current density of the PdAg catalyst is higher than that of the pure Pd and commercial Pd/C catalysts, suggesting that the PdAg catalyst had better long-term stability for ethanol electrooxidation.

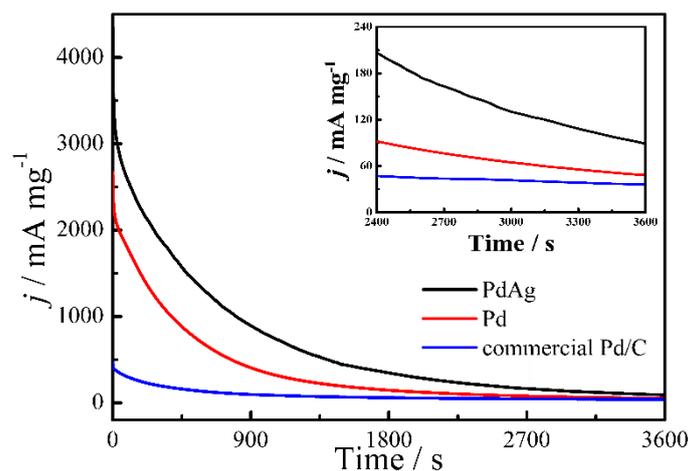


Figure 5. Chronoamperograms of the as-prepared catalysts for 1.0 M C₂H₅OH on 1.0 M KOH solution at −0.3 V.

EIS spectra of the PdAg catalyst are recorded in Figure 6, which can be used to assess the kinetics of the PdAg catalyst for ethanol oxidation reactions. In Figure 6A, the diameter of the impedance arc (DIA) on the PdAg catalyst decreased with the potential increasing from −0.6 to −0.3 V, which indicates that the ethanol oxidation rate increased owing to the fact that the carbonaceous intermediates generated from ethanol dehydrogenation were removed by oxidation [33]. As the potential continued to increase, the impedance arc reversed to the second quadrant at −0.25 V and −0.20 V, because of the removal of the intermediate species (such as CO_{ads}) generated on the surface of the catalyst and the recovery of the catalytic active sites. At the potential of −0.15 V, the impedance arc turned back to the first quadrant with a large diameter, which is mainly due to the formation of Pd oxides under the high electrode potential [34].

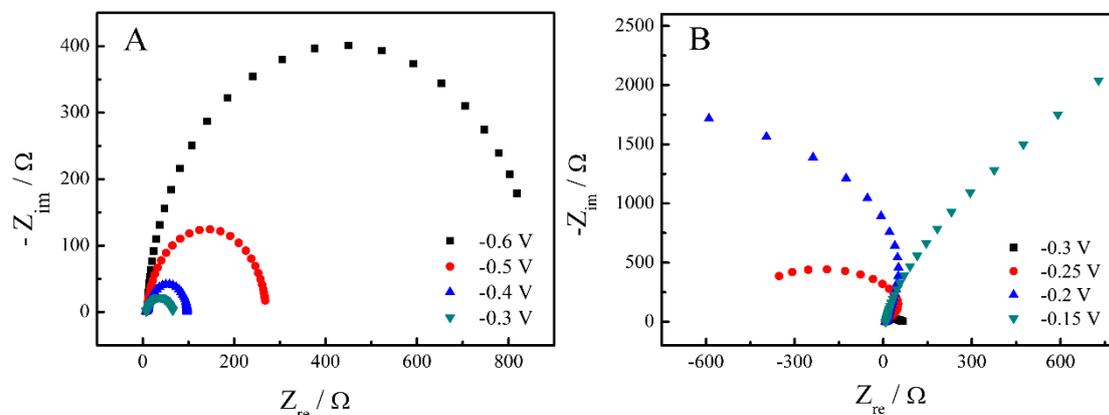


Figure 6. Nyquist plots of C₂H₅OH electrooxidation on the PdAg catalyst in 1.0 M C₂H₅OH + 1.0 M KOH solution with potential range of −0.6 V to −0.3 V (A), and −0.3 V to −0.15 V (B).

The PdAg-, Pd- and commercial Pd/C-modified GCE were investigated by EIS in 1.0 M KOH and 1.0 M C₂H₅OH at -0.3 V, and the Nyquist plots are displayed in Figure 7. As seen in Figure 7, all these catalysts exhibit a semicircle at high frequencies. The DIA of the PdAg catalyst is smaller than that of the pure Pd and commercial Pd/C catalysts, indicating the smaller charge-transfer resistance (R_{ct}). This result also demonstrates that the electron transfer rate on PdAg is faster than that on pure Pd and commercial Pd/C catalysts, which is consistent with the higher catalytic activity of PdAg catalyst.

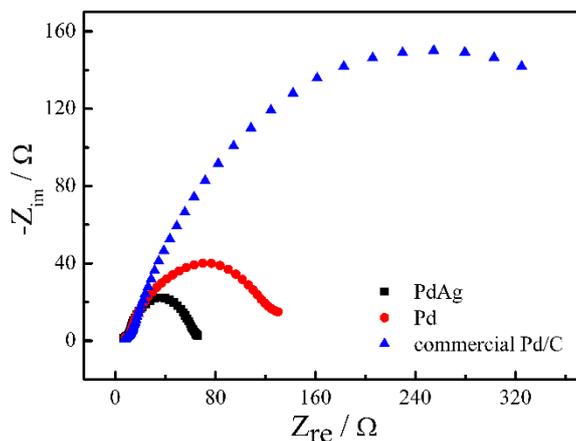


Figure 7. Nyquist plots of PdAg, Pd and commercial Pd/C for ethanol oxidation in 1.0 M C₂H₅OH + 1.0 M KOH solution with potential of -0.3 V.

3. Materials and Methods

3.1. Materials and Instruments

Palladium acetate (Pd(C₂H₃O₂)₂) was purchased from J&K Scientific Co., Ltd, Beijing, China, silver nitrate (AgNO₃), dimethyl formamide (DMF), NaBr, C₂H₅OH, KOH, and polyvinylpyrrolidone (PVP, K30) were all supplied by Sinopharm Chemical Reagent Co., Ltd, Shanghai, China, using without further purification. Commercial Pd/C catalyst (containing 20% Pd) were obtained from Shanghai Hesens Electric Co., Ltd, Shanghai, China. Doubly distilled water was used in the whole experiment.

The electrocatalytic experiments were performed using a CHI 760D electrochemical analyzer (CH Instrument, Inc, Shanghai, China). The three-electrode setup was made up of a saturated calomel electrode (SCE), a Pt wire and a modified glassy carbon electrode (GCE, diameter of 3 mm). The SCE, Pt wire and GCE worked as reference, counter electrode and working electrode, respectively. Before testing, the GCE was polished with α -Al₂O₃ powders (Tianjin AIDA hengsheng Science-Technology Development Co., Ltd., Tianjin, China, 0.05 m), washed with doubly distilled water and ethanol, then dried in the oven at 60 °C. Cyclic voltammetry (CV) measurement was used to analyze the activity of the as-prepared catalysts for ethanol electrooxidation, while the amperometric i-t curves obtained under -0.3 V was used to detect the long-term stability of as-prepared catalysts.

3.2. Synthesis of Nanochain PdAg Catalyst

The nanochain structure PdAg catalyst was prepared via hydrothermal method at 160 °C, using DMF as a reducing agent. The preparation procedure is as following: 7 mL DMF was added into a Teflon autoclave, 60 mg PVP, 20 mg NaBr, 3 mg AgNO₃ and 3 mL doubly distilled water were all added to the DMF solution, and the mixture was stirred under room temperature for 10 min. An orange mixture was formed gradually. Then, the mixture was heated to 160 °C from room temperature, keeping for 6 h and cooling down to room temperature naturally. Finally, the black solid product was obtained by centrifugation and thoroughly washed with water and ethanol several times.

For comparison, pure Pd catalyst was also prepared under the same condition according to the above preparation steps.

3.3. Preparation of Pd and PdAg Modified Electrodes

The working electrodes modified with Pd and PdAg catalysts were prepared as following: Firstly, the obtained black precipitates were dispersed in 9 mL doubly distilled water and 1 mL C₂H₅OH. After ultrasonic homogenization, the catalysts suspension was obtained. Then, 10 L catalysts “ink” was dripped onto the surface of the pretreated GCE. Finally, the modified GCE was dried at 60 °C in the oven. The mass loading of Pd for both the PdAg catalyst and pure Pd catalyst coated on the GCE is 2.37 mg.

3.4. Characterization

X-ray diffraction (XRD) (Philips, X'Pert-Pro MRD, Amsterdam, Netherland) profiles of the as-synthesized catalysts were obtained at 40 kV and 30 mA with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$), using glass slide as substrate, which are used to analyze the crystalline structure of the as-prepared catalyst. Transmission electron microscopy (TEM) images were taken on a TECNAI-G20 electron microscope (FEI Tecnai G2 F20 S-TWIN TMP, Hongkong, China), which are operated at 200 kV. The scanning electron microscope (SEM) (Hitachi Corporation, S-4700, Tokyo, Japan) equipped with energy-dispersive X-ray analyzer (EDX) (Hitachi Corporation, Tokyo, Japan) was applied to characterize the morphology and composition of the as-synthesized catalysts. The electrochemical impedance spectrometry (EIS) spectra were measured in 1.0 M C₂H₅OH alkaline solution between 1 and 10⁵ Hz, and the AC voltage amplitude is 5.0 mV.

4. Conclusions

In conclusion, the PdAg catalyst was prepared by a facile one-step hydrothermal method at 160 °C, using DMF solution as a reducing agent. The SEM, TEM and XRD characterization results have confirmed that the as-prepared catalyst is PdAg alloy and it has a nanochain structure. The electrochemical results have demonstrated that the catalytic activity and stability of the obtained PdAg catalyst for ethanol electrooxidation in alkaline media were remarkably enhanced because of the special structure of the catalyst and the introduction of the Ag element to the Pd catalyst.

Supplementary Materials: The following are available online at www.mdpi.com/2073-4344/6/7/103/s1, Figure S1: Cyclic voltammograms of PdAg catalysts with different molar ratio in 1.0 M C₂H₅OH/1.0 M KOH solution with scan rate of 50 mV s⁻¹. Figure S2: SEM image of PdAg catalyst prepared with NaBr (A), without NaBr (B). Figure S3: Typical N₂ adsorption-desorption isotherm of the as-prepared PdAg catalyst.

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Author Contributions: Yue Feng, Ke Zhang and Yukou Du conceived and designed the experiments; Yue Feng performed the experiments; Yue Feng, Bo Yan and Shumin Li analyzed the data; Yue Feng wrote the paper.

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

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