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Pt₃Ag alloy wavy nanowires as highly effective electrocatalysts for ethanol oxidation reaction

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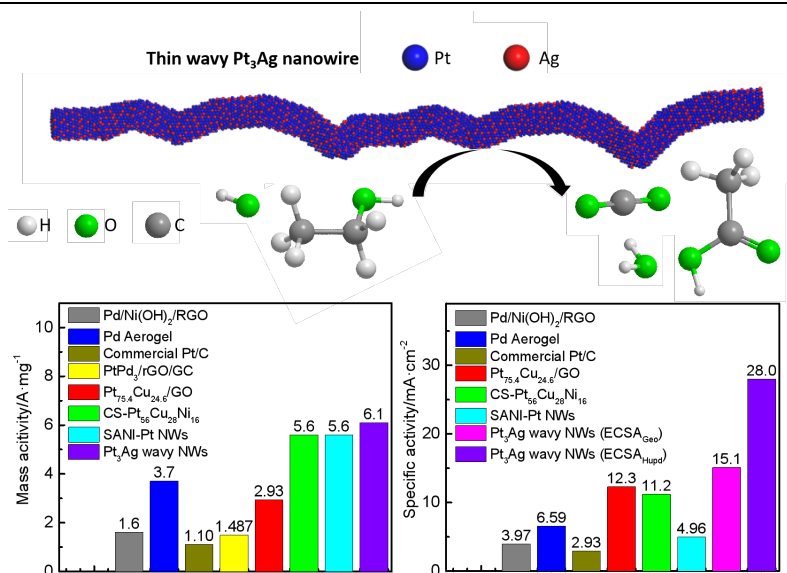
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Pt₃Ag alloy wavy nanowires were synthesized via a facile solvothermal method via particle attachment mechanism, which can function as high effective electrocatalysts for ethanol oxidation reaction with an ultrahigh mass activity of 6.1 A/mg.

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ABSTRACT

Direct ethanol fuel cell (DEFC) has received tremendous research interests because of the more convenient storage and transportation of ethanol vs. compressed hydrogen. However, the electrocatalytic ethanol oxidation reaction typically requires precious metal catalysts and is plagued with relatively high over potential and low mass activity. Here we report the synthesis of Pt₃Ag alloy wavy nanowires via a particle attachment mechanism in a facile solvothermal process. Transmission microscopy studies and elemental analyses show highly wavy nanowire structures with an average diameter of 4.6±1.0 nm and uniform Pt₃Ag alloy formation. Electrocatalytic studies demonstrate that the resulting alloy nanowires can function as highly effective electrocatalysts for ethanol oxidation reactions (EOR) with ultrahigh specific activity of 28.0 mA/cm² and mass activity of 6.1 A/mg, far exceeding that of the commercial Pt/carbon samples (1.10 A/mg). The improved electrocatalytic activity may be partly attributed to partial electron transfer from Ag to Pt in the Pt₃Ag alloy, which weakens CO binding and the CO poisoning effect. The one-dimensional nanowire morphology also contributes to favorable charge transport properties that are critical for extracting charge from catalytic active sites to external circuits. The chronoamperometry studies demonstrate considerably improved stability for long term operation compared with the commercial Pt/C samples, making the Pt₃Ag wavy nanowires an attractive electrocatalyst for EOR.

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1 Introduction

Compared with compressed hydrogen, alcohols have higher volumetric energy density and gravimetric energy density if we take the weight of the hydrogen tank into account [1]. In addition, they are also easier and intrinsically safer for storage and transport, making them attractive candidates for fuel cells [1]. Among the various alcohol fuel cells, ethanol has higher volumetric energy and gravimetric energy density than methanol, more importantly it also has the advantage for being much less toxic and produced renewable at lower cost [1]. Specifically, the alkaline direct ethanol fuel cell (ADEFC) is attracting increasing research interests recently [2]. In alkaline environment, the kinetics of cathode oxygen reduction reaction (ORR) becomes more favorable, which provides us with the choices of cheaper ORR electrocatalysts, such as AlN [3], ZrN [4] and many non-precious metal-based nanomaterials [5]. The reversed direction of the electro-osmotic drag also lowers the ethanol crossover in the cell, leading to higher efficiency [2]. The disadvantage of voltage drop caused by the CO_3^{2-} formation can be alleviated by changing electrolyte periodically or increasing operation temperature [6, 7]. However, the ethanol oxidation reaction (EOR) is kinetically much more difficult compared with the hydrogen oxidation reaction (HOR), and often requires precious metal-based electrocatalysts. Currently, Pt [8] and Pd [9] are the most widely studied catalyst materials for EOR, but still limited by relatively high overpotential, poisoning and low mass activity. Therefore, developing noble metal based electrocatalysts with high mass activities (defined as electrocatalytic performance normalized by the mass loading of the noble metal) is of great importance for cost-effective direct ethanol fuel cells.

In general, the mass activity of an electrocatalyst is determined by the product of the specific activity (SA) and electrochemical active surface area (ECSA). To enhance the specific activities, the surface modification remains to be the most common way, including creating alloys and hybrids materials. For example, Ru [10, 11], Ni [12] or $\text{Ni}(\text{OH})_2$ [13, 14] have been employed as highly oxophilic components to modify Pt or Pd and facilitate the formation of surficial -OH group, which is beneficial for the removal of the carbonaceous species on the nearby noble metal sites via the Langmuir-Hinshelwood mechanism.

Ag has also been suggested as a beneficial component to modify Pt and has received tremendous research interests for several reasons. Ag itself has the highest specific conductivity among all metals, which is intrinsically beneficial for electrocatalysis since charge transport is essential for electrocatalysis [15]. Additionally, Ag not only intrinsically binds weakly to CO as shown from the volcano plot (like Cu and Au from the same group) [16], but also helps adjust the d-band structure and enrich the local electron density around Pt upon alloying, which lowers the electron donation from CO to Pt and thus potentially weakens CO chemisorption and mitigates undesirable poisoning effect [17, 18]. Very recently, theoretical study suggested that the Pt_3Ag alloy with (111) crystal surface can facilitate the C-C bond cleavage during ethanol oxidation reaction [19], thus delivering a higher efficiency of utilizing ethanol as a fuel. Therefore, it is expected the Pt_3Ag alloy may be a good candidate for electrocatalytic ethanol oxidation reaction with improved SA.

Apart from increasing the SA, the enhancement of ECSA is also essential for enhancing the overall MA. To this end, the use of ultrafine nanostructures is important. However, ultrafine nanoparticles are usually not very stable under aggressive electrochemical reaction conditions due to the physical movement/aggregation and Oswald ripening processes. The one-dimensional (1D) nanowires is less mobile, more stable and less subjected to these drawbacks [20]. Thus, ultrathin nanowires represents an attractive class of electrocatalysts that can deliver ultrahigh ECSA [20, 21]. For the nanowires with wavy morphologies (wavy nanowires), the wavy surface with rich surface defects may also provide additional catalytic hotspots for further improved activity [22, 23]. Lastly, the 1D structure is also believed to have an intrinsic advantage to facilitate charge transport for more efficient utilization all available catalytic sites.

Here we report the synthesis of the Pt_3Ag wavy nanowires through a particle attachment mechanism in a facile solvothermal process. Transmission microscopy studies and elemental analyses reveal highly wavy nanowire structure with an average diameter of 4.6 ± 1.0 nm and uniform Pt_3Ag alloy formation. Electrocatalytic studies demonstrate that the alloy wavy nanowires may function as high effective electrocatalysts for ethanol oxidation reactions (EOR) with an ultrahigh SA (28.0 mA/cm^2) and a highest mass activity of 6.1 A/mg , far exceeding that of the commercial Pt/carbon samples (1.10 A/mg).



2 Experimental

2.1 Chemicals

Potassium tetrachloroplatinate (IV) (K_2PtCl_4 , 98%), silver nitrate (AgNO_3 , analytical grade), polyvinylpyrrolidone (PVP, MW. ~55000), concentrated ammonium hydroxide ($\text{NH}_3\cdot\text{H}_2\text{O}$, 28.0%–30.0%), sodium borohydride (NaBH_4), ethanol, acetone, ethylene glycol (EG, anhydrous, 99.8%) and the commercial platinum carbon (20%) were all used as received without further purification.

2.2 Synthesis of Pt₃Ag wavy nanowires

160 mg PVP were dissolved into 4 mL of EG after ultrasonication at first. And 0.018 mmol of K_2PtCl_4 and 0.006 mmol AgNO_3 were dissolved in 1.0 mL and 0.25 mL DI water, respectively. Then we uniformly mixed the aqueous solution of the Pt and Ag precursors with the EG solution of PVP in turn. The vial was then heated at 210 °C for 4 h. After cooling to room temperature, we added 0.7 mL concentrated ammonia water and 2 mL of aqueous solution of NaBH_4 (5.0 mg) for cleaning. After 1 hour, the products were collected via centrifugation after the addition of acetone and then washed with water for 2 times and ethanol for 2 times. Finally they were dispersed in ethanol for further study.

2.3 Structural characterizations

The X-ray diffraction (XRD) was tested on a Panalytical X'Pert Pro X-ray Powder Diffractometer with $\text{Cu-K}\alpha$ radiation after drop-casting the ethanol dispersion of Pt₃Ag wavy nanowires onto the glassy substrate and dried under room temperature. X-ray photoelectron spectroscopy (XPS) tests were carried out with Kratos AXIS Ultra DLD spectrometer after drop-casting ethanol dispersion of the sample on the silicon substrate and then dried. Transmission electron microscopy (TEM) images were carried out on an FEI T12 transmission electron microscope operated at 120 kV. High resolution TEM images (HRTEM) were taken on FEI Titan transmission electron microscope operated at 300 kV. The STEM image and EDS (energy dispersive x-ray spectroscopy) mapping were carried out on Joel Jem-300CF (Grand Arm) operated at 300 kV. The samples were prepared by dropping ethanol dispersion of the sample onto the carbon-coated copper TEM grids. The Pt loading of Pt₃Ag wavy nanowires on the GCE was determined by the inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

2.4 Electrochemical measurements

All the electrochemical studies were carried out via a three-electrode cell system. The working electrode was a glassy carbon electrode (GCE) with a geometry area of 0.196 cm² and the counter electrode was a Pt wire. We used Hg/HgO (1 M KOH) as the reference electrode for electrochemical test in alkaline media and Ag/AgCl as the reference electrode in acidic media. All the potential are converted against RHE. In order to fabrication the working electrode, the Pt₃Ag wavy nanowires were homogeneously dispersed in EtOH after sonication and 10.0 μL of the ink was drop-cast onto the surface of the electrode surface and dried at room temperature. The Pt loading of our nanowires on the electrode determined from ICP-AES was 2.10 μg (10.7 $\mu\text{g}/\text{cm}^2$ as normalized by the geometric area of the GCE).

To activate the electrocatalysts, cyclic voltammetry (CV) tests were performed in Ar-saturated 0.5 M H_2SO_4 electrolyte with a scan rate of 50 mV/s ranging from 0.05 V to 1.0 V vs. RHE. The electrochemical active surface area determined from hydrogen under potential deposition ($\text{ECSA}_{\text{Hupd}}$) was calculated by integrating hydrogen desorption charge using the constant of 210 $\mu\text{C}/\text{cm}^2$ for the hydrogen monolayer on platinum. The electrocatalytic ethanol oxidation reaction (EOR) tests were carried out in Ar-saturated 1 M KOH + 1 M EtOH electrolyte with potential scan rate of 50 mV/s in the range from 0.05 V to 1.1 V vs. RHE. To test the long term performance of the electrocatalysts, the chronoamperometry (CA) tests were carried out at 0.72 V vs. RHE for 6000 s. Commercial platinum carbon was used as control and 1.00 mg commercial Pt/C (20%) was mixed with 0.99 mL ethanol and 10.0 μL of Nafion (5 wt%) to prepare the ink after ultrasonication. And 5.0 μL of the Pt/C catalyst ink was drop-cast onto the GCE and dried to ensure a platinum loading of 1.0 μg (5.1 $\mu\text{g}/\text{cm}^2$) on the working electrode to ensure similar background current during CV scan. For the CA tests, the Pt-loading of Pt/C is 2.0 μg (10.2 $\mu\text{g}/\text{cm}^2$) by drop casting 10.0 μL of the Pt/C catalyst ink. All the electrochemical tests were carried out under the same conditions for the controlled sample of commercial Pt/C (20%).

3 Results and discussion

3.1 Characterizations of Pt₃Ag wavy nanowires

The morphologies of the wavy Pt₃Ag nanowires were studied by transmission electron microscope (TEM). TEM image clearly demonstrates ultrafine wavy nanowire geometry with diameters mainly in the range of ~3–6 nm and lengths exceeding 300 nm (Fig. 1(a)). The high-resolution TEM shows clearly

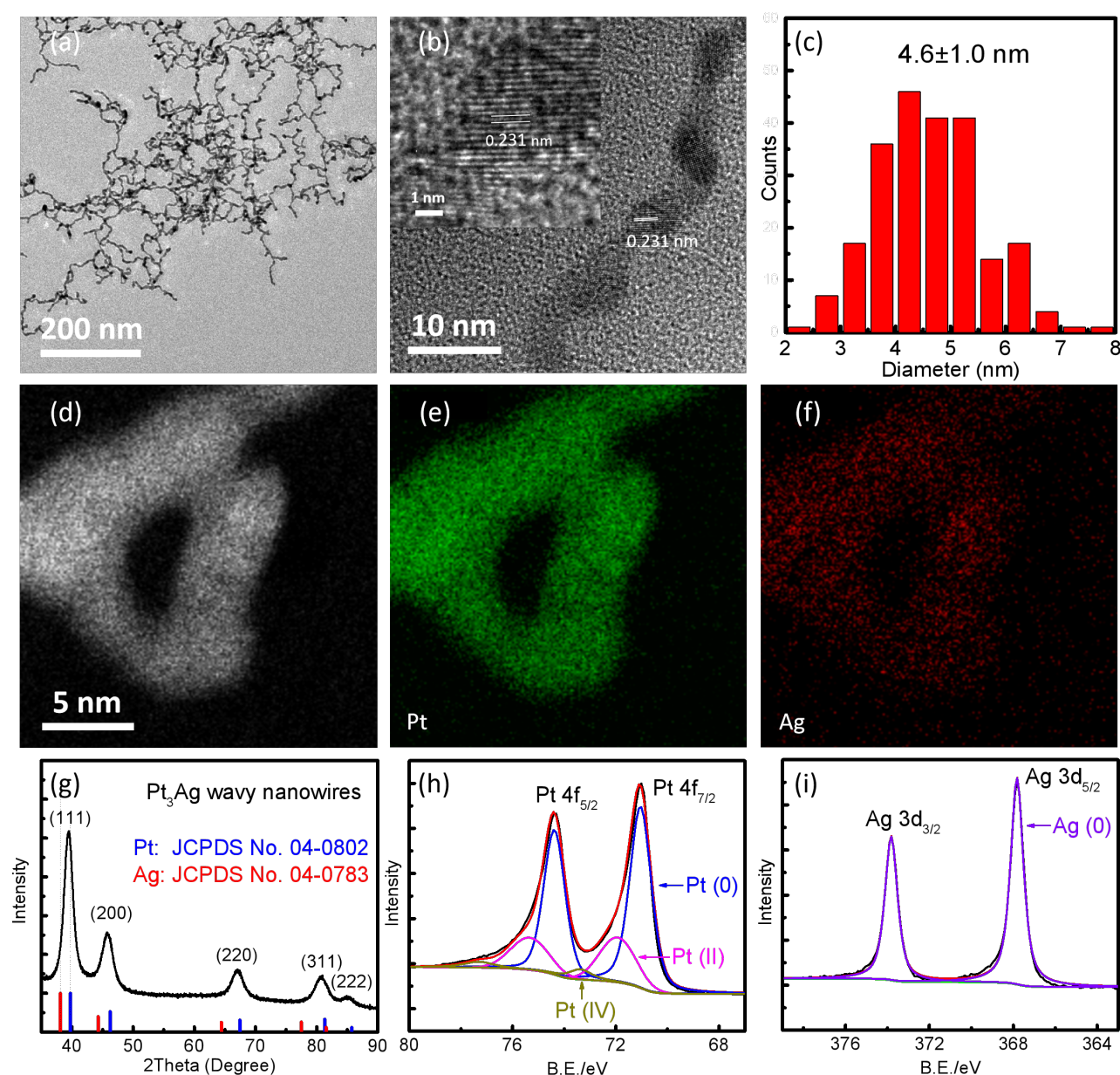


Figure 1 Structural characterizations of the thin wavy Pt_3Ag nanowires: (a) TEM image. (b) HRTEM image. (c) Diameter-distribution of nanowires. (d) Selected area for EDS mapping. (e) EDS mapping of Pt element. (f) EDS mapping of Ag element. (g) XRD characterization. (h) XPS characterization for Pt element. (i) XPS characterization for Ag element.

resolved lattice fringes with a lattice spacing of 0.231 nm (Fig. 1(b) and inset). This value falls between the lattice spacing of the (111) crystal planes of FCC Pt (0.227 nm) and FCC Ag (0.236 nm), indicating the formation of FCC alloys between Pt and Ag, which is also generally consistent with previous reports about the alloys between platinum and silver [24, 25]. Similar to the previously reported wavy nanowires, there are also apparently many surface defects, which may function as the catalytic active sites and contribute to the electrocatalytic performances according to the previous reports about wavy

nanowires [22, 23]. More importantly, the exposed (111) crystal plane of Pt_3Ag is also believed to help with C-C bond cleavage during EOR based on the previous theoretical study [19]. A statistical analysis of the diameters of the wavy nanowires reveal an average diameter of 4.6 ± 1.0 nm (Fig. 1(c)). Such small diameter is beneficial for boosting the ECSA.

To evaluate the alloy formation and elemental distribution within the wavy nanowires, we have conducted scanning transmission electron microscopy (STEM) studies and elemental mapping statues using energy dispersive X-ray spectroscopy

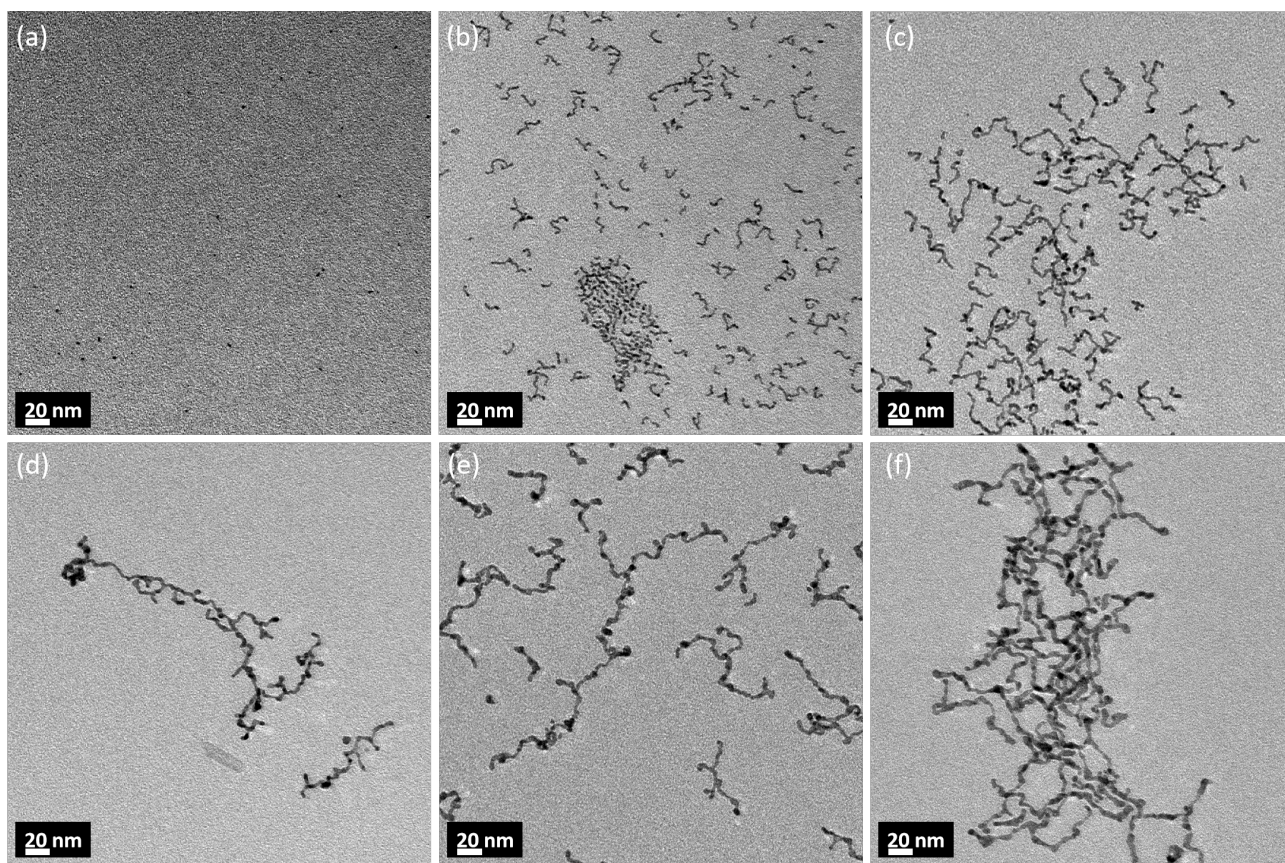


Figure 2 TEM pictures of reaction intermediates collected at different time intervals: (a) 1 min (b) 5 min, (c) 10 min, (d) 20 min, (e) 30 min and (f) 60 min.

(EDS) (Fig. 1(d)-(f)). The EDS mapping demonstrates that uniform distributions of platinum and silver throughout the wavy nanowires, confirming the formation of uniform alloy. The ratio of Pt: Ag determined from EDS analysis is 2.76:1 as shown in Fig. S1 in Electronic Supplementary Material (ESM), which also agrees well with the results from ICP-AES (2.83:1) and the feed ratio of the precursors (3:1), further confirming the composition of the alloy wavy nanowires.

Fig. 1(g) shows the XRD pattern of the Pt₃Ag wavy nanowires sample. Compared with the standard XRD pattern of the FCC silver (JCPDS No. 04-0783) and FCC platinum (JCPDS No. 04-0802) whose characteristic peaks are attributed to the (111), (200), (220), (311) and (222) crystal planes, the Pt₃Ag nanowires also show the same set of peaks attributed to (111), (200), (220), (311) and (222) crystal plane positioned exactly between those of Pt and Ag, further confirming the formation of uniform alloys, which is also consistent with the observations from HRTEM and EDS mapping. By applying Scherrer's equation for these peaks, the size of the crystallites

was estimated to be 4.3 nm, which generally agrees with the observations from TEM. In Fig. 1(h) and (i), the XPS results demonstrate the composition and valence of the surface platinum and silver species in Pt₃Ag nanowires. The peaks at the binding energies (BE) of 71.0 and 74.4 eV correspond to the 4f_{7/2} and 4f_{5/2} of the Pt (0), respectively [24, 25]. The peaks at the BE of 71.9 eV and 75.3 eV correspond to the 4f_{7/2} and 4f_{5/2} of the Pt (II) [24, 25] while the peaks at the 73.4 eV and 77.3 eV correspond to the 4f_{7/2} and 4f_{5/2} of the Pt (IV) species [26]. These oxidized Pt species might be attributed to the oxidized surficial Pt in air or the unreacted precursor. The peak area ratio of 4f_{7/2} and 4f_{5/2} follows the theoretical value of 4:3 for all split peaks of Pt(0), Pt (II) and Pt (IV) and the content of Pt (0) is calculated as 70.2% based on the peak area. For silver, the peaks at the BE of 367.8 and 373.8 eV correspond to the 3d_{5/2} and 3d_{3/2} of the Ag (0) following the theoretical value of 3:2. The absence of other split peaks indicates that the silver exists predominately as metallic Ag (0).

We also find that the BE for the Pt 4f orbits are comparably lower than those of commercial Pt/C as

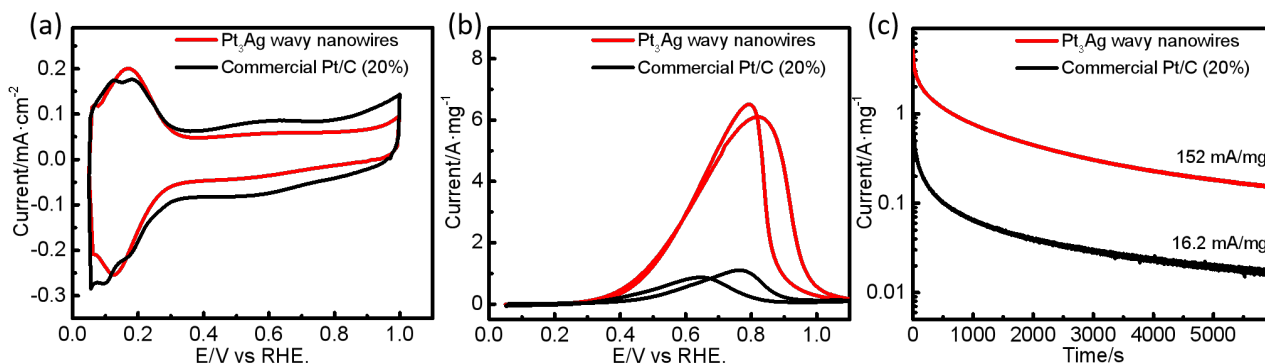


Figure 3 (a) CV curves of the thin wavy Pt₃Ag wavy nanowires (Pt loading: 10.7 $\mu\text{g}/\text{cm}^2$) and commercial Pt/C (20%) (Pt loading: 5.1 $\mu\text{g}/\text{cm}^2$) electrocatalysts in 1 M KOH electrolyte at scan rate of 50 mV/s. (b) Mass-normalized CV curves of the thin wavy Pt₃Ag wavy nanowires and commercial Pt/C (20%) electrocatalysts in 1 M KOH + 1 M EtOH electrolyte at scan rate of 50 mV/s. (c) Chronoamperometry results of the thin wavy Pt₃Ag wavy nanowires (Pt loading: 10.7 $\mu\text{g}/\text{cm}^2$) and commercial Pt/C (20%) (Pt loading: 10.2 $\mu\text{g}/\text{cm}^2$) electrocatalysts in 1 M KOH+1 M EtOH electrolyte at 0.72 V vs. RHE.

shown in Fig. S2 in the ESM with Pt (0) 4f_{7/2} shifted from 71.3 eV to 71.0 eV and Pt (0) 4f_{5/2} shifted from 74.6 eV to 74.4 eV upon alloying with silver, indicating the electronic states of Pt are adjusted due to the electron donation from silver (electronegativity: 1.93) to platinum (electronegativity: 2.28). It has been proposed that the negatively shifted BE indicates enriched electron density of Pt, which could weaken the interaction with lone electron pair of CO and other carbonaceous species, and thus lowers the binding and poisoning effect [18, 27]. Accordingly, silver also has higher BE when compared with pure Ag NWs with Ag (0) 3d_{5/2} shifted from 367.4 eV to 367.8 eV and Ag (0) 3d_{3/2} shifted from 373.4 eV to 373.8 eV, which further confirms the electron transfer from Ag to Pt [28].

In our synthesis of the Pt₃Ag wavy nanowires, EG works as the reducing agent under high temperature while PVP works as the template agent to help forming wavy nanowires via the particle attachment mechanism. Similar synthetic system for wavy nanowire growth has also been reported with PVP as the template agent previously [23]. In addition, PVP will also help with the exposure of the (111) crystal plane of the noble metals, which is important for many catalytic reactions [29, 30] including EOR [19].

To further reveal the growth mechanism, we have also taken TEM pictures of the products collected at the different reaction intervals (Fig. 2). At $t=1$ min, there are lots of tiny crystallites (~ 2 nm) formation. As the reaction time goes, there are short nanorods beginning to form ($t=5$ and 10 min), followed by the formation of longer nanowires ($t=20, 30$ and 60 min). This observation also agrees with the previous literature about the particle attachment mechanism for wavy nanowire growths [23, 24].

3.2 Electrocatalytic ethanol oxidation reaction

We have first conducted electrochemical cyclic voltammetry (CV) to determine the ECSA_{Hupd} of the Pt₃Ag wavy nanowire catalysts (Fig. 3(a)). In the 0.5 M H₂SO₄ electrolyte, the forward scan demonstrates the characteristic hydrogen desorption region while the reverse scan exhibits the characteristic hydrogen adsorption region. The ECSA_{Hupd} was calculated to be 21.8 m²/g by using the constant of 210 $\mu\text{C}/\text{cm}^2$ for the hydrogen monolayer. While the ECSA_{Hupd} of commercial platinum carbon was calculated to be 37.5 m²/g. The regions corresponding to oxygen desorption and adsorption were very weak since it is not a highly favorable process in acidic media compared with alkaline media.

The theoretical surface area (ECSA_{Geo}) for 1D Pt nanowires with average diameter of 4.6 nm is expected to be ~ 40.5 m²/g by using the geometrical model of thin and long circular cylinder with only lateral area taken into consideration. The smaller ECSA observed in experiments might be attributed to the introduction of Ag on the surface, which is inactive towards the hydrogen underpotential deposition and may partially block the Pt sites [24].

The catalytic activity of the Pt₃Ag nanowires for EOR was carried out in the electrolyte of 1 M KOH and 1 M ethanol (Fig. 3(b)). The forward scan demonstrates a strong current peak at the potential of 0.81 V vs. RHE, corresponding to the oxidation of ethanol with a peak mass activity of 6.1 A/mg. This mass activity is not only 5.5-fold higher than the commercial Pt/C (20%) (1.10 A/mg), but also higher than those of the most previously reported Pt and Pd-based electrocatalysts as shown in Fig. 4(a) (Single atom Ni-Pt NWs [21], Core-shell Pt₅₆Cu₂₈Ni₁₆ tetrahedral [31], Pt_{75.4}Cu_{24.6}/RGO [32], PtPd₃/rGO/GC

[33], Pd/Ni(OH)₂/RGO [13] and Pd Aerogel [34]), indicating a great utilization efficiency of the noble metal. In addition, the Pt₃Ag wavy nanowire electrocatalysts also have a more negative shifted onset over-potential (defined as the over-potential required to reach a MA of 0.1 A/mg according to the previous literature [21]) at 0.30 V when compared with the commercial Pt/C (20%) at 0.41 V, suggesting our alloy nanowires also have lower activation barrier for ethanol oxidation reaction.

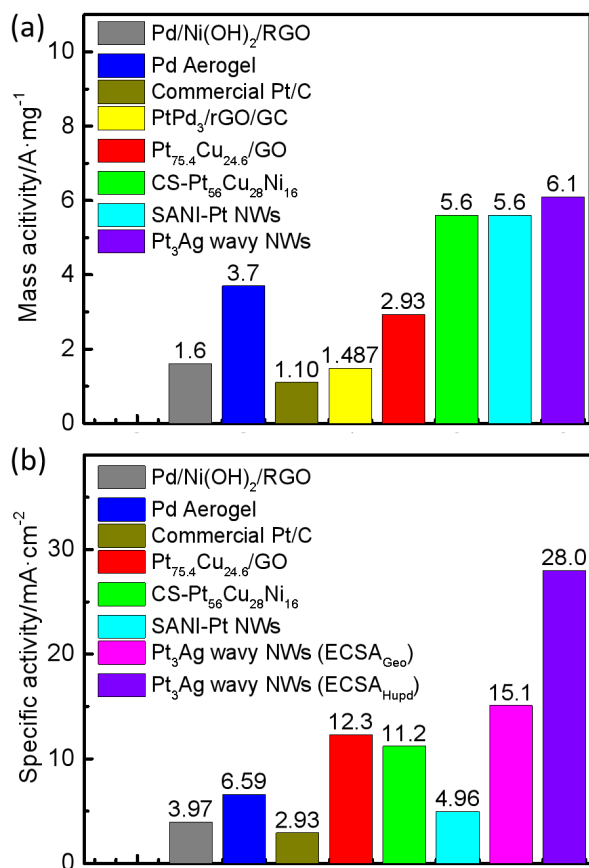


Figure 4 The comparisons of EOR performances of our thin Pt₃Ag alloy wavy nanowires with the previously reported Pt and Pd-based electrocatalysts tested in alkaline media in terms of: (a) Mass activity. (b) Specific activity.

The specific activity is calculated as 28.0 mA/cm² based on the ECSA_{Hupd}. Considering that the ECSA_{Hupd} may be underestimated, we may calculate the SA as 15.1 mA/cm² by using the geometrical surface area (ECSA_{Geo} ~40.5 m²/g), which is still much higher than most of the previous literatures as shown in Fig. 4(b) (Single atom Ni-Pt NWs [21], Core-shell Pt₅₆Cu₂₈Ni₁₆ tetrahedron [31], Pt_{75.4}Cu_{24.6}/RGO [32], Pd/Ni(OH)₂/RGO [13] and Pd Aerogel [34]). Such high SA might be attributed to the formation of the Pt₃Ag alloy since the introduction of silver alters the band structure of

platinum and lowers the electron donation with CO and other carbonaceous species thus mitigates the binding and the poisoning effect [17], in addition to that Ag also binds very weakly towards CO. Finally according to the recent theoretical studies, the (111) crystal plane of Pt₃Ag alloy can also help cleaving the C-C bond during ethanol oxidation reaction [19], to ensure a more efficient utilization the energy in ethanol. Therefore, we can tentatively conclude that the ultrahigh mass activity of the Pt₃Ag wavy nanowires largely arise from the ultrahigh SA since the ECSA of the wavy nanowire is moderate due to the relatively thick diameter compared with the previously reported ultrathin nanowires.

In the reverse scan, the anodic peak has a negative potential shift and slightly higher peak current compared with those in the forward scan. However, this reverse scan peak should be no longer attributed to the oxidation of the residue carbonaceous species [35, 36] after the previous forward scan and the I_F/I_R ratio should not be a criterion to evaluate the CO-tolerance ability of the electrocatalyst [37]. Instead, according to the most recent literature about Pt electrocatalyst, during the forward scan, the rate-determining-step (RDS) is the water dissociation step and after the forward scan the Pt will be oxidized at high potential, causing a change in the surface and covered with the oxygenated species. Then during the reverse scan, the RDS will be changed to the alcohol dehydrogenation step due to oxygenated Pt surface, leading to different peak potential and peak current in the reverse scan [35, 37].

For our electrocatalyst, it is noted that during the CVs in alkaline electrolyte (without ethanol), our Pt₃Ag nanowires have much less reactivity to oxygen adsorption and desorption compared with the commercial Pt/C (Fig. S3 in the ESM), indicating that it is comparably less susceptible to surface oxide formation during the forward scan and more easily to recover during the backward scan. As a result, the backward scan would be less impacted by oxygenated Pt surfaces after the forward scan. Therefore, the backward scan exhibits a more similarly high current and more similar peak position to those of the forward scan (I_F/I_R=0.94, ΔE_p=0.02 V). In comparison, commercial Pt/C has much higher tendency to form a layer of surficial oxide, as indicated by CV in alkaline media, causing the backward scan to go into the alternate pathways and a more evident change in the peak potential and peak current during the backward scan (I_F/I_R=1.26, ΔE_p=0.13 V). This similar phenomena and explanations have also been reported with PtNi

electrocatalysts before [38].

Finally, the chronoamperometry tests (Fig. 3(c)) were carried out to evaluate the long term performance of the Pt₃Ag wavy nanowire electrocatalyst. The Pt₃Ag wavy nanowire can maintain a current of 152 mA/mg at 0.72 V vs. RHE after 6000 s. In sharp contrast, the commercial Pt/C only maintain a mass activity of 16.2 mA/mg at 0.72 V vs. RHE after 6000 s, indicating that Pt₃Ag nanowires has much improved long term performance when compared with the commercial Pt/C, demonstrating our Pt₃Ag nanowires have much higher stability apart from much higher mass activity, which mainly attributes from the introduction of Ag to enrich the electron density to weaken the chemisorption of the carbonaceous species [17, 39] and the relatively higher stability of the 1D nanowires under harsh electrochemical conditions compared with its 0D counterparts [20]. Meanwhile, we also find that the catalytic activity can be generally recovered after 25 cycles of CV scanning after each CA test. For example, after 10 rounds of repeated CA tests, the nanowires still maintain a high mass activity of 112 mA/mg (Fig. S4 in the ESM).

4 Conclusion

In summary, we have successfully synthesized Pt₃Ag wavy nanowires via a particle attachment mechanism in a facile solvothermal process. The resulting Pt₃Ag wavy nanowires can function as highly effective EOR electrocatalysts with an extraordinary specific activity of 28.0 mA/cm² and an ultrahigh mass activity of 6.1 A/mg, considerably higher than most of the previously reported Pt and Pd-based electrocatalysts in alkaline media, which is largely attributed to the formation of Pt-Ag alloy and electron transfer from Ag to Pt. Furthermore, the Pt₃Ag wavy nanowires also show significantly improved stability, and thus can promise a highly effective electrocatalyst for EOR

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Electronic Supplementary Material: EDS spectrum of Pt₃Ag alloy wavy nanowires, XPS comparison between Pt₃Ag alloy wavy nanowires and Pt/C, CV activation in alkaline media, and long term CA test (10 cycles of 6000s) of the electrocatalysts is available in the online version of this article at http://dx.doi.org/10.1007/s12274-***.***.*** (automatically inserted by the publisher.).

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Electronic Supplementary Material

Pt₃Ag alloy wavy nanowires as highly effective electrocatalysts for ethanol oxidation reaction

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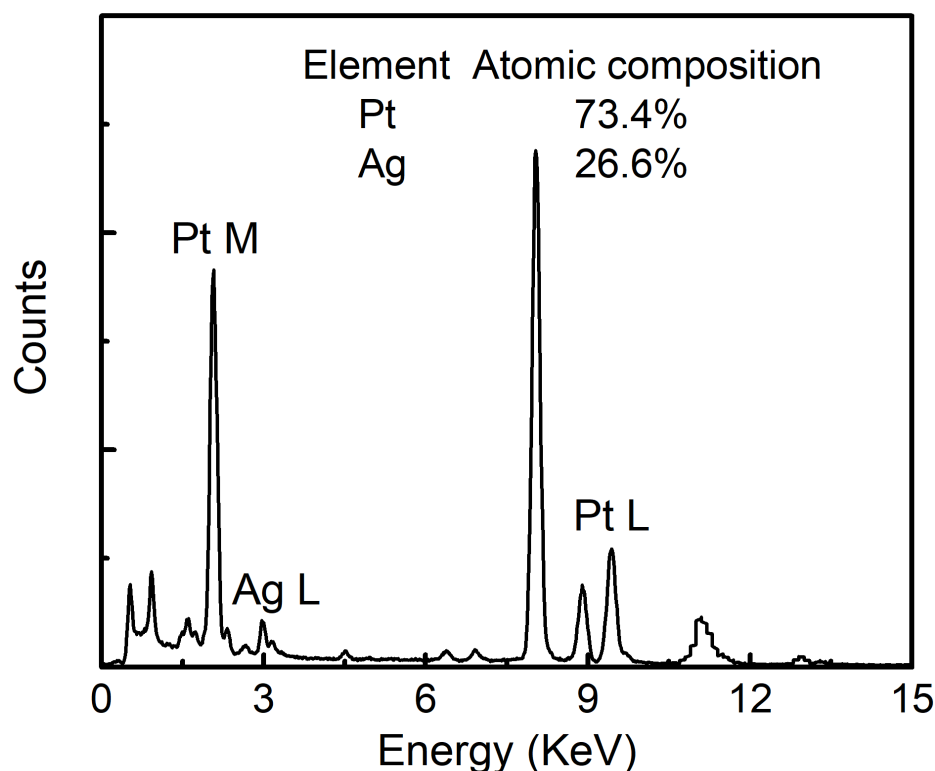


Figure S1 EDS spectrum and elemental composition of the thin alloy Pt₃Ag wavy nanowires.

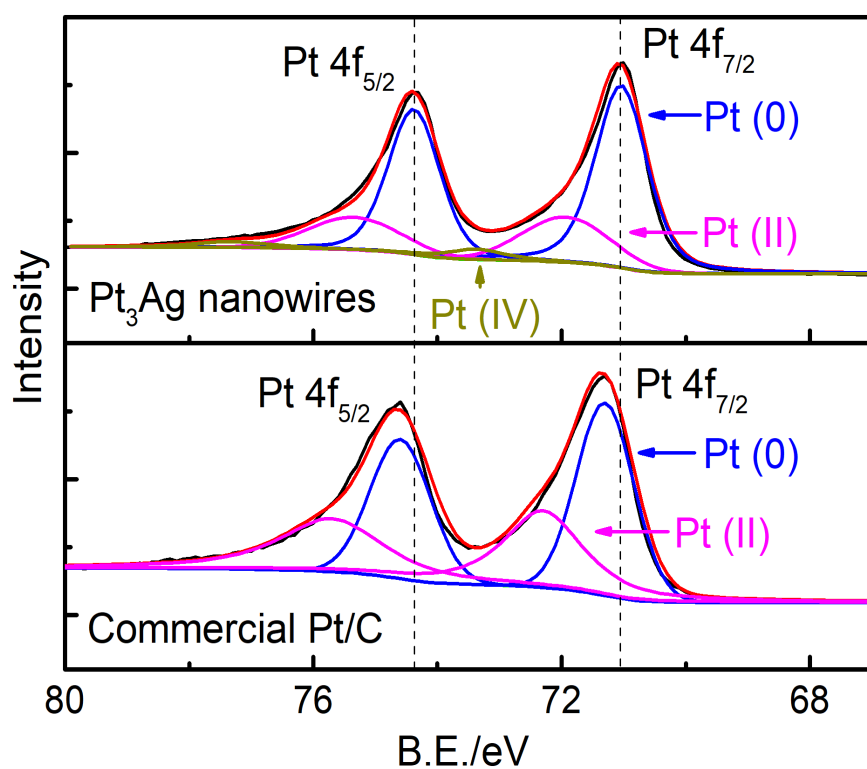


Figure S2 Comparison between the XPS (Pt element) of the Pt_3Ag nanowires and the Pt/C.

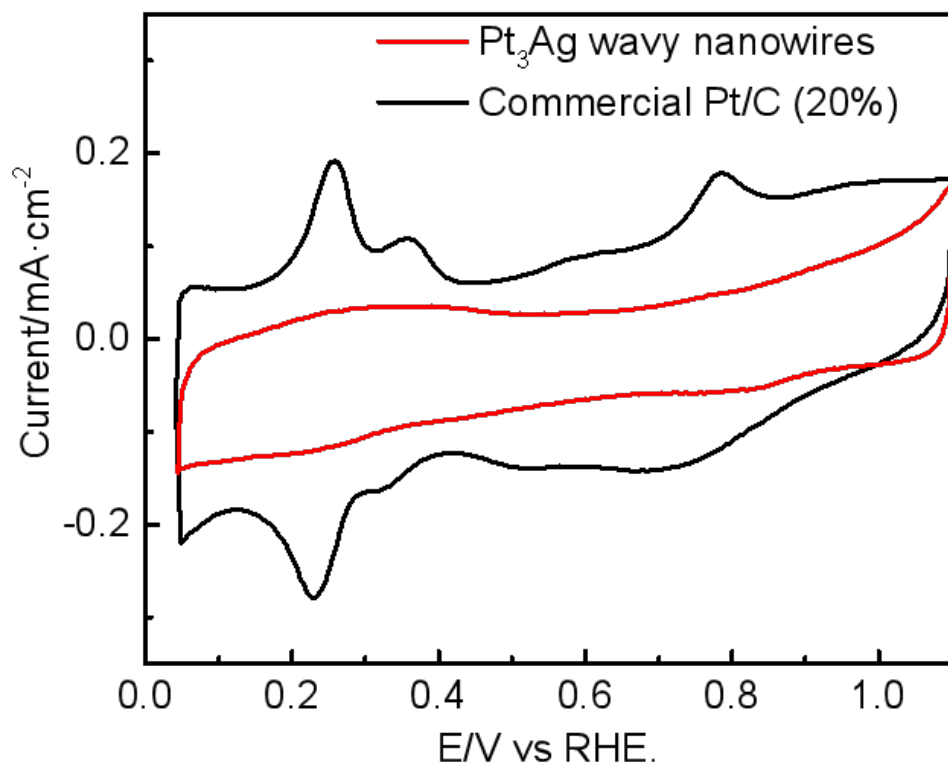


Figure S3 CVs of Pt_3Ag wavy nanowires and commercial Pt/C in 1 M KOH electrolyte at the scan rate of 50 mV/s.

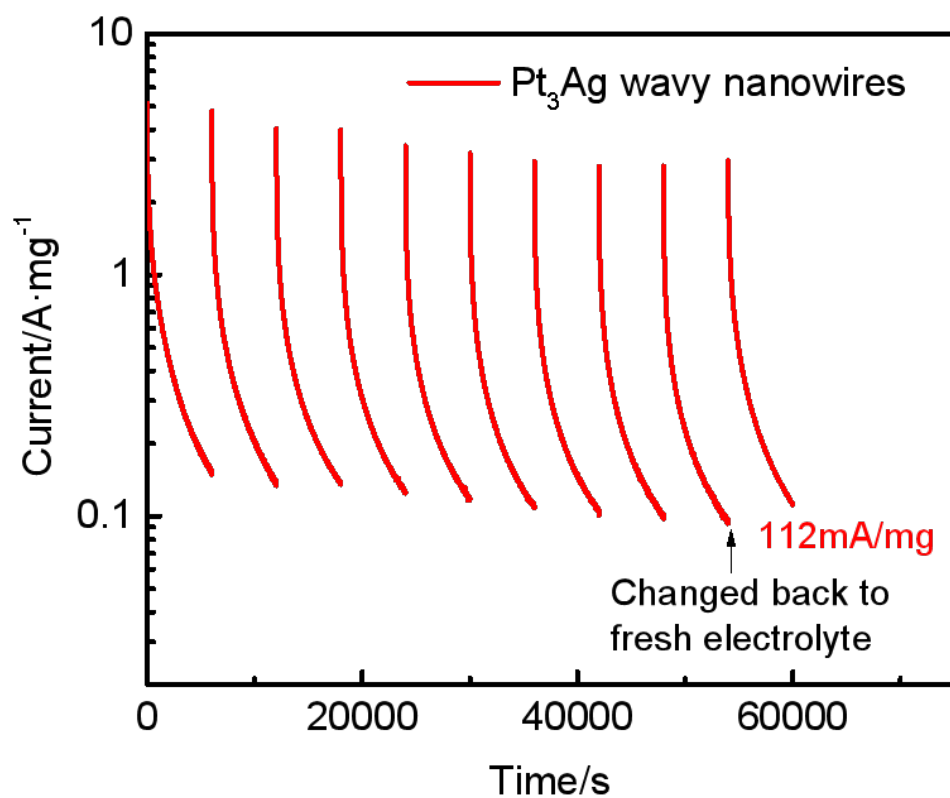


Figure S4 10 consecutive cycles of chronoamperometry tests of Pt₃Ag wavy nanowires with 25 cycles of CV scanning (50 mV/s) between each two CA tests in the electrolyte of 1 M KOH+ 1 M EtOH. (Electrolyte changed back to the freshly prepared after the 9th cycle).