Hollow Ag@Pd core–shell nanotubes as highly active catalysts for the electro-oxidation of formic acid

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Abstract

Ag nanowires are prepared as templates by a polyol reduction process. Then Ag nanotubes coated with a thin layer of Pd are synthesized through sequential reduction accompanied with the galvanic displacement reaction. The products show a hollow core–shell nanotubular structure, as demonstrated by detailed characterizations. The Ag@Pd can significantly improve the electrocatalytic activity towards the electro-oxidation of formic acid and enhance the stability of the Pd component. It is proposed that the enhanced electrochemically active surface area and modulated electron structure of Pd by Ag are responsible for the improvement of electrocatalytic activity and durability. The results obtained in this work are different from those previous reports, in which alloy walls with hollow interiors are usually formed. This work provides a new and simple method for synthesizing novel bimetallic core–shell structure with a hollow interior, which can be applied as high-performance catalysts for the electro-oxidation of formic acid.

Online supplementary data available from stacks.iop.org/Nano/23/105609/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction

Polymer electrolyte membrane (PEM)-based fuel cells are generally considered to be viable candidates to replace batteries as portable power sources. Traditionally, direct methanol fuel cells (DMFCs) are the dominant choices. However, despite many years of intensive research, inherent limitations still remain, such as innate toxicity, sluggish anodic oxidation kinetics and the fuel crossover problem in Nafion® based membranes [1]. Therefore, there is an increasing need to search for an alternative fuel with which these problems can be avoided. Formic acid, a non-flammable liquid at room temperature and a non-toxic chemical, can be a good substitute for methanol. Previous studies have reported that formic acid can be oxidized at less positive potential and with faster kinetics than methanol at room temperature, and the crossover effect of formic acid through the polymer membrane is lower than that of methanol [2, 3].

For a good electrocatalyst, both the high electrocatalytic activity and the low cost must be taken into account to meet the practical applications. In the previous research, platinum appeared to be a promising catalyst which had the highest catalytic activity among the anode catalysts for electro-oxidation of methanol or formic acid [4]. Unfortunately, the surface of Pt was usually heavily poisoned by the strong adsorption of CO produced during the oxidation of fuels,
resulting in the derogation of catalytic performance [5]. Based on the so-called bifunctional mechanism [6, 7], Pt-based nanomaterial electrocatalysts had been investigated for enhanced electrocatalytic activity towards formic acid oxidation (FAO) including Pt–Pd [8], Pt–Au [9], Pt–Ag [10] and especially Pt–Ru [11]. However, due to the high cost and the limited world supply of platinum, research interest had been devoted to the development of platinum-free electrocatalysts, among which palladium-containing catalysts were proved to be effective candidates [12, 13]. The activity of Pt/C was still not satisfactory, and more importantly, the durability was in urgent need of further improvement because this catalyst deactivated quickly [14]. It is commonly accepted that the catalytic activity and stability can be improved by the addition of another metal, such as Pd–Au [15–17], Pd–Co [18, 19] and Pd–Ag [20]. Another effective method of enhancing catalytic activity is by designing porous, hollow or core–shell structures, in which the specific surface area of the catalyst can be increased significantly or the electron structure can be modulated to a certain extent [21, 22].

In this work, Ag@Pd core–shell nanotubes were synthesized by the successive reduction, also known as the seed-mediated growth method. Galvanic displacement could not be avoided during this process, which was responsible for the formation of the hollow structure. The unsupported Ag@Pd nanotubes were used as the anode catalyst for formic acid oxidation. Electrochemical measurements showed that the as-synthesized catalyst had excellent electrocatalytic activity and durability towards the FAO. To the best of our knowledge, this is the first time that hollow tubular core–shell structure Ag@Pd was synthesized and used as a catalyst for the electro-oxidation of formic acid.

2. Experimental section

2.1. Materials

Silver nitrate (AgNO₃, ≥99.8%, Beijing Chemical Reagent), palladium (II) nitrate dihydrate (Pd(NO₃)₂·2H₂O, ≥39.5% w/w (cont. Pd), Sinopharm Chemical Reagent Co., Ltd), palladium black (99.9%, Alfa Aesar), poly(vinyl pyrrolidone) (PVP, Mₕ ≈ 55 000, Aldrich), ethylene glycol (EG, AR grade, Beijing Chemical Reagent), sulfuric acid (H₂SO₄, AR grade, Tianjin Chemical Reagent) and formic acid (HCOOH, AR grade, Beijing Chemical Reagent) were used as received. All aqueous solutions were prepared with ultra-pure water (>18.3 MΩ cm) from a Milli-Q Plus system (Millipore).

2.2. Synthesis of core–shell Ag@Pd nanotubes

Hollow core–shell Ag@Pd nanotubes were prepared by sequential reductions [23]. Ag nanowires were first synthesized according to a modified polyol process described before [24, 25], then Pd salts were reduced in the presence of Ag nanowire seeds in the sequential reduction. Briefly, 0.24 M PVP (in terms of repeating units) dissolved in 5 ml EG was preheated to 160°C under vigorous stirring. Then 2.5 ml portion of freshly prepared AgNO₃ solution (0.08 M in EG) was added in a dropwise fashion into the hot PVP solution using a syringe at a rate of approximately 0.15 ml min⁻¹. Afterwards, the reaction mixture was continued with heating at 160°C for another 60 min. After the solution was cooled to room temperature, the mixture was centrifuged at a low rate for 5 min to eliminate some Ag nanoparticles (if any) which may be formed in the process. The final mixture was diluted with ethanol and centrifuged, then washed with ethanol for several times. The as-obtained Ag nanowires were dissolved in 20 ml EG while stirring. The obtained colloidal solution was then mixed with a solution containing 0.006 g Pd(NO₃)₂·2H₂O, 0.12 g PVP and 20 ml EG. The resulting solution was heated (approx. 7°C min⁻¹) to 90°C for 2 h under a N₂ atmosphere. The obtained Ag@Pd nanotubes were precipitated in acetone, washed with acetone twice and dried under a N₂ atmosphere.

2.3. Characterizations

Transmission electron microscopy (TEM) images were obtained using a JEOL 2000 transmission electron microscope operating at 200 kV. Scanning electron microscopy (SEM) pictures were imaged by a field emission scanning electron microscopy (FE-SEM, XL30ESFM-EG). High-resolution transmission electron microscopy (HRTEM) images and the corresponding live fast Fourier transform (FFT), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images, element analysis mapping and energy-dispersive x-ray spectroscopy (EDX) were carried out on a JEM-2010 (HR) microscope operated at 200 kV. Inductively coupling high frequency plasma mass spectrophotometry (ICP-MS) was used to further analyze the content of the elements. X-ray diffraction (XRD) spectra were obtained by a D8 ADVANCE (Germany) using Cu Kα radiation with a Ni filter (λ = 1.5406 Å at 30 kV and 15 mA). The UV–vis absorption spectra were collected using a Cary 500 scan UV/vis/NIR spectrophotometer.

2.4. Electrochemical investigations

Electrochemical experiments were performed with a CHI 660A electrochemical workstation in a conventional three-electrode system. The working electrode was a 3 mm glassy carbon electrode (GCE) covered with the catalyst samples. A platinum wire and a Ag–AgCl (3 M KCl) electrode were used as the counter electrode and the reference electrode, respectively. All of the potentials were quoted with respect to the Ag–AgCl electrode (3 M KCl). Before use, the GCE was carefully polished to a mirror finish with 1.0, 0.3 and 0.05 μm alumina slurries, successively. 2 mg of dried Ag@Pd nanotubes, Ag nanowires or the Pd black were dispersed in 0.9 ml pure water and 100 μl 5% Nafion solution by ultrasonication for a few seconds. Then 10 μl of the homogeneous catalyst ink was dropped onto the clean electrode and allowed to dry in vacuum at room temperature. The supporting electrolyte was 0.5 M H₂SO₄ with and without 0.5 M HCOOH depending on the test requirements. For CO-stripping measurements, the catalyst surface was first saturated with CO by bubbling CO through 0.5 M H₂SO₄.
while holding the working electrode at open circuit potential for 20 min. The electrode was quickly moved to a fresh solution and the linear sweep voltammetry was tested at a scan rate of 10 mV s\(^{-1}\).

3. Results and discussion

3.1. Structure characterization of the Ag@Pd

The UV–vis absorption spectra showed the characteristic absorption of Ag nanowires in figure 1(a). The Ag nanowires had a main absorption at 388 nm with a shoulder at 352 nm. These two absorption bands, as reported previously [26, 27], were ascribed to the surface plasmon resonance bands of the transverse and longitudinal modes of the silver nanowires, respectively. The UV–vis absorption of Ag nanowires synthesized here also agreed well with those of Ag nanowires or nanorods reported previously [28, 29]. After the sequential reduction of Pd salt on Ag nanowire seeds, however, the surface plasmon resonance peaks of the Ag nanowires were damped out almost completely by the deposition of Pd, indicating the effective formation of a thin layer of a palladium shell on the Ag nanowire seeds. This will be demonstrated further in other characterizations.

To examine the crystallinity of the initial Ag nanowires and the Ag@Pd, powder x-ray diffraction measurements were recorded in figure 1(b). The JCPDS data of Ag (no. 03-0921) and Pd (no. 01-1201) were also given for comparison. The diffraction peaks of Ag nanowires accorded well with the JCPDS data. It was interesting to note that the XRD pattern of Ag@Pd presented mostly the features of Ag nanowires, except for an obvious peak of Pd(111) and an inconspicuous shoulder peak of Pd(200). The results suggested that the crystalline lattice of the synthesized Ag@Pd was dominated from the silver component. Generally, the core of a bimetallic core–shell structure can be detected by XRD because the diameter of the core is usually large enough to give significant diffraction peaks. However, whether the diffraction information of the shell is detectable or not depends on the thickness of the shell [30–33]. For example, in the case of the Au@Pd core–shell structure, the Pd shell with a thickness of 0.8 nm was too thin to make significant diffraction peaks of 3 nm could be seen distinctly [34, 35]. In the present prepared Ag@Pd structure, there may be some thick Pd shells that can give diffraction peaks, which can contribute to the shoulder peak of Pd(111) and Pd(200).

Figures 2 and 3 presented representative TEM and SEM images of the as-synthesized Ag nanowires and Ag@Pd nanostructure with different magnifications. As shown in figures 2(a), (b), 3(a) and (b), the Ag nanowires were solid with smooth surfaces and had diameters of approx. 80 ± 5 nm and lengths of longer than 5 \(\mu\)m. After the Pd salts were reduced and deposited on the Ag seeds, the structure changed into hollow nanotubes with coarse surfaces yet the dimension of the Ag@Pd nanotubes had not changed much (seen from figures 2(c), (d), 3(c) and (d)). The surface roughness could be ascribed to the poor epitaxial growth of Pd on Ag due to the relatively large difference (≈4.8%) in lattice constant between Ag and Pd. It should be noticed that the as-synthesized Ag@Pd nanotubes were fragile, so ultrasonication treatment should be controlled to a few seconds to retain their intact structure. When the Ag@Pd nanotubes were sonicated for more than 30 s, some tubes were prone to rupture at certain sites with hollow interiors (shown in figure S1 available at stacks.iop.org/Nano/23/105609/mmedia), indicating that the formation of tubular segments decreased the mechanical strength of these nanowires.

The fine structures of the Ag@Pd nanotubes were further characterized using HRTEM. Figures 4(a) and (b) showed the HRTEM images of one nanotube at different positions. It can be seen that the Ag@Pd nanotubes indeed had a hollow structure with a thin layer (approx. 6–8 nm) of Pd. From a closer observation, as shown in figure 4(c), it was found that the Pd shell deposited on the nanotubes had a single crystalline structure. Further measurements showed that there was mainly one type of lattice fringe with an interplanar spacing of 2.24 Å in the shell region, which was ascribed to the Pd(111). The distance measured between the two nearest atom rows for the inner Ag lattice was 2.32 Å, corresponding to the Ag(111) plane. The corresponding FFT pattern of the Ag@Pd nanotubes demonstrated that it was single crystalline with sixfold rotational symmetry (inset of figure 4(b)).

The distribution of Ag and Pd elements in the nanotubes was studied by the HAADF-STEM. Figure 5 presented a representative STEM image of the Ag@Pd nanotubes and the corresponding Ag and Pd elemental maps. As shown in
Figure 2. TEM images of the original Ag nanowires (a), (b) and the subsequently synthesized Ag@Pd nanotubes (c), (d) with different magnifications.

figures 5(b) and (c), the Ag and Pd were both detectable and concentrated in the periphery of the structure, accounting for the hollow tubular structure. However, the Pd signal was somewhat wider than that of Ag, indicating the hollow core–shell structure in all probability. The cross-sectional compositional line profiles in figures 5(d) and (e) clearly revealed the hollow structure, as the intensities in the center were distinctly weaker than those in the shell regions. We could further conclude the Ag-core and Pd-shell structure of the Ag@Pd nanotubes since the intensity of Pd was dramatically large at the shell region, where there was hardly detectable signal of Ag. From the contrast of the two signals at the shell region, it can also be estimated that the shell had a thickness of several nanometers. The element composition of the Ag@Pd nanotubes was examined by EDX (figure 5(f)). There were both distinct peaks from Ag and Pd, except for the Cu signals rooted in the supported grids. ICP-MS analysis showed that the mass ratio of Pd to Ag was determined to be 10:90.

It was necessary to investigate the formation process of the unique hollow core–shell nanotubular structure. Here the sequential reduction of Pd salts on the seeds of the Ag nanowires and the galvanic replacement may work at the same time. It is recently reported that Ag–Pd core–shell nanoparticles can be easily prepared by sequential reductions in ethylene glycol using Ag nanoparticles (~8 nm in diameter) as the seeds [23]. By applying the similar sequential reduction approach to the Ag nanowire seeds, however, galvanic replacement occurred at the same time and played an important role in the synthesis of hollow core–shell nanotubes. Previous reports had investigated the formation of bimetallic nanostructures with hollow interiors in an aqueous solution by galvanic replacement reaction extensively and intensively [25, 36, 37]. This water-based synthetic route was also extended successfully to organic media. For example, Yang et al reported that Ag–Au core–shell nanoparticles were obtained from the replacement reaction between 9.6 nm Ag nanospheres and dodecylamine-hydrophobized HAuCl₄ in toluene [38]. The results also ruled out the formation of Ag–Au alloy nanoshells with hollow interiors, which usually obtained for the replacement reaction between Ag nanoparticles and AuCl₄⁻ in aqueous solution [25, 37]. Replacement reactions in chloroform and o-dichlorobenzene were also reported [39, 40]. In this work, the obtained results had differences from these previous reports, in which alloy walls with hollow interiors were usually obtained. However, the replacement reaction should take place in a similar way. It was demonstrated in previous work that the major requirement to form hollow structures with seamless shells in the replacement reaction seemed to be the use of templates...
Figure 3. SEM photographs of Ag nanowires (a), (b) and the Ag@Pd nanotubes (in a back-scattered electrons, BSE mode) (c), (d).

with sufficiently large dimensions (>20 nm) [25, 39]. The Ag nanowires used in this work commendably satisfied this requirement.

Similar to the situation in the aqueous solution, the replacement reaction occurs because the standard reduction potential of Pd$^{2+}$/Pd was higher than that of Ag$^+/Ag$. Based on the previous research of galvanic replacement reactions in both aqueous and organic solvents, the probable mechanism for the formation of core–shell nanotubes was proposed. In general, the galvanic replacement between Ag nanowire templates and Pd(NO$_3$)$_2$ involves a number of processes, including diffusion of Pd$^{2+}$ to the surface of Ag templates, deposition of Pd atoms on the surface of templates and, at the same time, oxidation of Ag to Ag$^+$, as well as atomic diffusion and structural redistribution. The reaction was like a corrosion process, with Ag being oxidized from some highest energy sites (anode reaction). The released electrons could easily transfer to the surface of the templates and reduced Pd$^{2+}$ to Pd. The reduced Pd atoms tended to deposit on the surface of the templates and the epitaxial deposition would lead to the formation of a thin layer of palladium, which prevented the Ag underneath from reacting with Pd(NO$_3$)$_2$, so the inner Ag served as active sites. At last, the hollow core–shell nanotubular structure Ag@Pd was formed. Figure 6 illustrated the probable replacement process. The sequential reduction of Pd salts with Ag nanowires as seeds also played a role for the formation of the Pd shell. Further studies with regard to the detailed reaction process will be investigated in our next work.

3.2. Performance of the synthesized Ag@Pd for formic acid electro-oxidation

Cyclic voltammetry measurements (CVs) were first carried out to characterize the electrochemical behavior of the hollow core–shell Ag@Pd nanotubes. Figure 7 depicted the typical CVs of the Ag@Pd, and the palladium black in N$_2$-saturated 0.5 M H$_2$SO$_4$ with the current density being normalized by the palladium loading. The peaks below 0.15 V were attributed to the hydrogen adsorption and desorption process, while those above 0.35 V were assigned to the oxidation of Pd to palladium oxide and the reduction of the oxides thus formed. The potential window between 0.15 and 0.35 V corresponded to the double-layer region. The CV characteristics of the modified electrodes had some difference from early reports for the bulk palladium electrode [41, 42], probably owing to the modulation of electron structure of Ag to Pd. The observation of separated hydrogen adsorption and desorption peaks, and the peaks at a more positive potential, suggested the large surface area of the Ag@Pd nanotubes, which was in accordance with the TEM images. It is known that the electrochemical surface area is one of the most important parameters to determine the catalytic activity for formic
The real surface area of Pd-based catalysts could be evaluated from the integrated charge of the hydrogen adsorption in the CV curve. The total charge $Q_H$ was calculated to be 21.9, 55.5 mC mg$^{-1}$ Pd for the Pd black and the Ag@Pd, respectively.

It should be noted that cyclic voltammetry measurements could provide forceful evidence for the formation of complete Ag@Pd core–shell structure, as CVs can be regarded as a surface-sensitive technology that only detect the electrochemical information of surface atoms rather than bulk atoms [44]. Figure S2 (available at stacks.iop.org/Nano/23/105609/mmedia) showed the CVs of the Ag nanowires in 0.5 M H$_2$SO$_4$, the anodic peak at approx. 0.45 V indicated the formation of silver oxides or Ag$^+$, while the cathodic peak in the reverse scan corresponded to the reduction of silver oxides. The current density response was comparable to that of Ag@Pd However, there was hardly the signal of Ag in the composite, indicating the formation of a complete shell around the Ag template.

To test the performance of the catalysts towards FAO, CVs on the Ag@Pd and Pd black electrodes were carried out in a mixed solution of 0.5 M H$_2$SO$_4$ and 0.5 M HCOOH at a scan rate of 50 mV s$^{-1}$ (figure 8). It could be seen that the Ag@Pd nanotubes had an activity more than twice as high than that of Pd black with the same Pd loading. For the Ag@Pd modified electrode, there was a broad peak with peak potential at 0.250 V along with a negligible shoulder at 0.8–1.0 V, which corresponded to the oxidation of formic acid via the direct pathway and the indirect pathway, respectively [45, 46]. The presence of a tiny oxidation current peak at a more positive potential suggested that there was little CO poisoning of the Ag@Pd in FAO. The current density ratio of the anodic oxidation peak ($J_a$) to the cathodic peak ($J_c$) was more than 1 ($J_a/J_c \approx 1.33$), and the potentials of the

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**Figure 4.** HRTEM images of the Ag@Pd nanotubes (a)–(c). The inset of (b) showed the corresponding two-dimensional fast Fourier transform (FFT) pattern.
Figure 5. Representative HAADF-STEM images (a) and the corresponding elemental maps of the Ag (b) and Pd (c). (d) Dark-field TEM images of the Ag@Pd nanotubes. (e) Cross-sectional compositional line profiles of the Ag@Pd. (f) EDX analysis of the Ag@Pd nanotubes.

forward scan oxidation peak and the reverse peak had little difference. These all indicated that the Ag@Pd nanocatalyst suffered little from deactivation and poisoning [47]. The Pd black in the control experiment showed similar characters as Ag@Pd. However, the current density was markedly smaller and the peak potential of FAO was more positive than that of the Ag@Pd.

The dual-pathway mechanism is widely accepted for FAO with Pt- or Pd-based catalysts. The most desirable pathway is via dehydrogenation, which does not form CO as an intermediate product (direct pathway). Another pathway via dehydration involves adsorbed CO as a poisoning intermediate species (indirect pathway). On the basis of previous reports [12, 32, 48, 49], and the results in this work, we propose the probable mechanism of the Ag@Pd for FAO as below:

For the direct pathway

\[
\text{HCOOH} + \text{Pd}^0 \rightarrow \text{CO}_2 + 2\text{H}^+ + 2e^- + \text{Pd}^0. \tag{1}
\]

For the indirect pathway

\[
\text{HCOOH} + \text{Pd}^0 \rightarrow \text{Pd} - \text{CO} + \text{H}_2\text{O} \tag{2}
\]

\[
\text{Pd} - \text{CO} + \text{Pd} - \text{OH} \rightarrow 2\text{Pd}^0 + \text{CO}_2 + 2\text{H}^+ + 2e^- \tag{3}
\]

\[
\text{Overall} : \text{HCOOH} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2e^- \tag{5}
\]

In order to know the kinetic characterization of FAO on Ag@Pd, the influence of the scan rates on the current response was also studied (figure S3 available at stacks.iop.org/Nano/23/105609/mmedia). The peak current increased linearly with the square root of the scan rates, as shown in figure S3 inset. This indicated that the electrocatalytic oxidation of formic acid on the Ag@Pd catalyst was a diffusion-controlled process.

CO-stripping voltammograms of the catalysts were also performed (figure S4 available at stacks.iop.org/Nano/23/105609/mmedia). A lower CO-stripping potential and the smaller area indicated a higher antipoisoning ability towards CO of the Ag@Pd catalyst [50]. The CO-stripping results together with the CV measurements indicated that the FAO on the Ag@Pd was mainly through the direct pathway due to its high CO tolerance. Consistently, as revealed by the chronoamperometric measurements (figure S5 available at stacks.iop.org/Nano/23/105609/mmedia), the Ag@Pd showed better stability and lower poisoning effect compared with the Pd black. It can be seen that the initial and steady-state current densities obtained from the Ag@Pd were much larger than those from the Pd black over the entire examined period, which agreed well with the CV tests in figure 8. The enhanced performance of the Ag@Pd catalyst can be attributed to three aspects: firstly, the thin shell structure of Pd on an Ag core with a rough surface increased the electrochemical active surface area of the catalyst, offering more active sites necessary for the FAO; secondly, the modulation of electronic structure of palladium by silver facilitated the electron transfer and the removal of poisoning intermediates on the catalyst. Besides, the superior activity of the Ag@Pd nanotubes network can be attributed to the
effective electronic transfer through the highly interconnected networks [51]. We are contemplating further improvements in the FAO performance through the optimization of the core size and the Pd loading.

4. Conclusions

In summary, Ag@Pd nanotubes were synthesized by means of sequential reduction together with galvanic replacement in ethylene glycol. Detailed characterization, such as TEM, HRTEM, EDX, SEM, XRD and electrochemical techniques demonstrated that the nanostructure indeed had a core–shell structure. The as-synthesized core–shell structure with a rough and thin shell of Pd showed enhanced catalytic activity and durability for formic acid oxidation than Pd black, as a result of modulated electron structure as well as improved Pd utilization. The FAO reaction on the catalyst was mainly...
through a direct pathway (dehydrogenation reaction) due to its increased CO tolerance. In addition, the nanotubes were well interconnected and did not require any support so that corrosion and detachment problems which often suffered in the nanoparticles/supporting systems can be avoided. The catalyst reported here had a novel structure, and the method could be easily applied to other metal systems for controlled synthesis of new bimetallic nanostructure. The core–shell Ag@Pd nanotubes had simple and clean processing, improved utilization of precious metals and desired catalytic properties, which suggested their great potential as efficient anode electrocatalysts for fuel cells.

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