Supportless oxygen reduction electrocatalysts of CoCuPt hollow nanoparticles

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This paper describes a facile solution route to the synthesis of CoCuPt hollow nanoparticles that readily form chain-like structures in solution. The formation of porous CoCuPt nanostructure is through galvanic replacement with cobalt-containing cores as the templates. This approach does not require the further removal of templates and greatly simplifies the synthetic procedures. These porous CoCuPt nanoparticles can be used as supportless electrocatalysts that exhibit enhanced mass- and area-specific activities in the oxygen reduction reaction (ORR) over commercial Pt black catalysts. The highest ORR specific activity achieved so far for this ternary Pt-alloy catalyst is 0.37 mA cm\(^{-2}\)Pt which is more than double that for Pt black.

Keywords: hollow structure; nanochain; CoCuPt; platinum alloy; oxygen reduction reaction; supportless

1. Introduction

Considerable attention has been paid to the development of alternative fuel and storage materials to address both environmental and energy concerns (Gasteiger et al. 2005; Chen et al. 2009; Gasteiger & Markovic 2009; Greeley et al. 2009; Peng & Yang 2009). A proton exchange membrane fuel cell (PEMFC) is a type of energy conversion device that does not rely on fossil fuels and thus can be an attractive solution (Gasteiger et al. 2005). They have also been investigated for applications as the energy conversion source for portable electronics (Shukla & Raman 2003; Teng et al. 2006). For PEMFCs, carbon-supported Pt (Pt/C) has been widely used as the electrocatalyst in the oxygen reduction reaction (ORR) at the cathode region, if hydrogen is used as the fuel. Both the stability and activity of such Pt/C catalysts, however, need to be improved (Gasteiger et al. 2005; de Bruijn et al. 2008).

Platinum alloys can be the choice of materials for improving the ORR catalytic properties while reducing the cost. PtM (M=Co, Fe, Ni) binary alloys are often several times more active than pure Pt metal (Casado-Rivera et al. 2004; Gasteiger et al. 2005; Srivastava et al. 2007; Chen et al. 2008b; Greeley et al. 2009; Peng & Yang 2009). Ternary Pt-based alloy catalysts such as CoCuPt show even better performance in the ORR than the PtM binary systems.

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(Srivastava et al. 2007). Besides activity, the stability of catalysts also needs to be improved to meet the requirements for practical applications. Among the degradation mechanisms of Pt/C catalysts, carbon corrosion is one of the major problems (de Bruijn et al. 2008). In this context, replacement or elimination of the carbon support is one possible approach. Hollow or porous structures made of small nanometre-sized catalysts that have high specific surface area could potentially be a viable solution (Liang et al. 2004a,b; Teng et al. 2006, 2007; Chen et al. 2007a,b, 2008a; Peng et al. 2010).

A widely used method for making hollow structures is based on the sacrificial templates that are made of polymers, metals, silica, and surfactant assemblies, such as vesicles and microemulsions (Bourlinos et al. 2001; Velikov & van Blaaderen 2001; Gao et al. 2002; Kim et al. 2002; Wong et al. 2002; Mayers et al. 2003; Sun et al. 2003; Yang et al. 2003; Vasquez et al. 2005; Yavuz et al. 2009). By removing the templates after the deposition of targeted materials, one can produce hollow structures. Recently, transmetallization and the nanometre-scale Kirkendall effect have been applied to make several interesting hollow structures from metal nanoparticles. Pt and PtCo hollow nanospheres can be made using Co nanoparticles as sacrificial templates, which could be completely or partially removed by the galvanic replacement or transmetallization reaction (Liang et al. 2004b; Vasquez et al. 2005). These synthesized Pt hollow nanospheres showed good electrocatalytic activity in the oxidation of methanol. Supportless hollow nanotubes of Pt and PtPd had much less relative loss in electrochemical surface area (ECSA) than Pt/C and Pt black catalysts after multiple cycles (Chen et al. 2007b). However, the types of hollow nanoparticles are still limited, especially for those Pt alloys that have a high ORR activity.

In this paper, we describe an efficient solution phase synthesis of porous CoCuPt hollow nanostructures. As demonstrated recently, this Pt ternary alloy can have a very high ORR mass activity and is an excellent targeted material for the development of hollow electrocatalysts (Srivastava et al. 2007). We show that CoCuPt hollow nanostructures, whose walls are composed of small grains, can be made in solution. These Pt ternary alloy nanostructures exhibit much enhanced oxygen reduction electrocatalytic activities, especially after annealing at a moderate temperature of about 200°C.

2. Experimental details

(a) Synthesis

A mixture of 10 mg of cobalt(II) chloride hydrate (CoCl2·xH2O, 99.999%, Aldrich, 0.077 mmol) and 250 mg of polyvinylpyrrolidone (PVP, MW: 1 300 000, Aldrich, 1.92 × 10⁻⁴ mmol) was dissolved in 50 ml of de-ionized water and sonicated for 15 min, followed by purging with argon gas for 15 min (Bourlinos et al. 2001). A solution of sodium borohydride (NaBH4, 99%, Aldrich, 0.13 mmol) in 10 ml of de-ionized water was added dropwise into the above mixture for 5 min while being stirred. After the solution turned dark brown, 13.8 mg of potassium tetrachloroplatinate(II) (K2PtCl4, 99.9%, Alfa Aesar, 0.13 mmol) and 3.8 mg of copper(II) sulphate (CuSO4, ≥99%, Aldrich, 0.024 mmol) in 15 ml of water were added dropwise for 3 min. This mixture was stirred for an additional 30 min.
at ambient room temperature. The precipitate was separated from the reaction mixtures by centrifuging at 6000 r.p.m. for 5 min and then dispersed in 120 ml of water. This process was repeated three times.

(b) Preparation of hollow CoCuPt electrocatalysts

The entire as-synthesized nanoparticles from a single batch were washed in 30 ml of ethanol, followed by centrifuging at 12 000 r.p.m. for 10 min. The precipitate was collected and then dispersed in 30 ml of ethanol, which was subjected to ultrasonication for 10 min. This process was repeated three times in order to remove PVP. These CoCuPt hollow nanoparticles were placed in a crucible and loaded into a quartz tube which was transferred into a tube furnace (Lindberg/Blue, Mini-Lite) for heat treatment at 200, 400, or 600°C in air for 10 min and then under a forming gas of 5 per cent hydrogen in argon for another 30 min. The ramping rate was set at 10°C min⁻¹ and the flow rate of the forming gas was kept at 50 ml min⁻¹.

(c) Characterization

Transmission electron microscopy (TEM) images were taken on an FEI TECNAI F-20 field emission microscope at an accelerating voltage of 200 kV. Scanning transmission electron microscopy (STEM) and elemental mapping were carried out under a high-angle annular dark field (HAADF) mode on the same microscope. Energy dispersive X-ray (EDX) analysis was carried out on a field emission scanning electron microscope (FE-SEM, Zeiss-Leo DSM982) that was installed with an EDAX detector. Powder X-ray diffraction (XRD) patterns were recorded using a Philips MPD diffractometer with a Cu Kα X-ray source (λ = 1.5405 Å). Isotherm and surface area measurements were carried out on an ASAP 2020 accelerated surface area and porosimetry analyser from Micromeritics. Nitrogen and helium were used as the analysing gases. Thermogravimetric analysis (TGA) was carried out using an SDT-Q600 TGA/DSC system from TA Instruments, Inc. The ramp rate was set at 10°C min⁻¹ and the gas flow rate was at 50 ml min⁻¹. The sample was heated from room temperature to 900°C in a predetermined gas atmosphere of either air or nitrogen and annealed at 900°C for 10 min.

Rotating disc electrode (RDE) measurement was conducted on a conventional three-electrode cell using a CHI760 dual channel electrochemical station (Garcia-Contreras et al. 2008). Platinum black (Alfa Aesar, HiSPEC 1000) was used as the reference catalyst. The catalyst ink was prepared by mixing 2.5 mg of CoCuPt hollow nanoparticles with 5 ml of Nafion solution (Fluka, Nafion 117 solution, 5%; water : propanol : 5% Nafion = 4 : 1 : 0.025). The amount of the catalyst was 10 μg of CoCuPt which was loaded onto the RDE using 20 μl of catalyst ink. The working electrode was a circular glassy-carbon disc (area: 0.196 cm²). A 1 x 1 cm² platinum foil was used as the counter electrode and a reversible hydrogen electrode (RHE, HydroFlex, Gaskatel) was the reference. The ECSA was determined based on cyclic voltammetry (CV) at room temperature. The CV was conducted in argon-saturated 0.1 M HClO₄ solution between 0 and 1.2 V (versus RHE) and at a scan rate of 50 mV s⁻¹. The ORR catalytic activity was measured in a 0.1 M HClO₄ solution that was purged with oxygen
for 30 min prior to, and during, the tests. The rate of the rotating disc was set at 1600 r.p.m. The forward potential was swept between 0 and 1.1 V (versus RHE) at 10 mV s$^{-1}$.

3. Results and discussion

Cobalt nanoparticles were used as the sacrificial templates for making the trimetallic hollow nanoparticles. Cobalt cations were reduced by NaBH$_4$ in aqueous solution using PVP as the capping agent to form Co nanoparticles. Figure 1 shows the nanoparticles collected after the reaction for 5 min and before the addition of Pt and Cu precursors. The average diameter of the nanoparticles made was about 21 ± 4 nm. These nanoparticles could form chain-like structures in solution during the synthesis (Kobayashi et al. 2003). While capping agents of surfactants are typically invisible under TEM, PVP could be observed on the surface of the nanoparticles.

To deposit Pt and Cu metals, K$_2$PtCl$_4$ and CuSO$_4$ solutions were added to the formed Co nanoparticle mixtures in a flask at room temperature after the reaction for 30 min. The two ionic metal precursors, [PtCl$_4$]$^{2-}$ and Cu$^{2+}$, reacted with the formed Co nanoparticles through the following galvanic replacement reactions:

\[
[PtCl_4]^{2-} + Co \rightarrow Pt + Co^{2+} + 4Cl^- \quad (3.1)
\]

and

\[
Cu^{2+} + Co \rightarrow Cu + Co^{2+} \quad (3.2)
\]

Figure 2a shows representative TEM images of hollow nanoparticles made at room temperature with a reaction time of 30 min. These hollow spheres had an average diameter of about 20 nm and a wall thickness of about 3 nm, thus an inner diameter of about 15 nm. Interestingly, these hollow nanoparticles formed chain-like structures. The walls of neighbouring hollow spheres appeared to be tightly connected or fused together. Such chaining behaviours have been previously observed for nanoparticles with magnetic cores. The formation of chain-like morphology suggests that cobalt was most probably reduced first and involved in the formation of magnetic cores at the early stage of the reaction. As cobalt is ferromagnetic and the formation of the monoxide layer could further increase the coercivity of the particles (Sorensen 2001), the chaining of nanoparticles should be largely due to the magnetic interactions. The formation of approximately 20 nm hollow structures further suggests Co metal should most probably form the cores. High-resolution (HR) TEM image shows the wall of the hollow spheres was composed of small crystallites with a typical diameter of about 2.5 nm (figure 2b). The lattice has a spacing of 0.224 nm, which matched well with the expected $d$-spacing of the (111) plane of CoCuPt alloy as the corresponding values are 0.205 nm for Co (111), 0.209 nm for Cu (111) and 0.227 nm for Pt (111) planes.

The structure and chemical composition of these hollow nanoparticles were further characterized based on both XRD and EDX. Figure 3a shows the XRD pattern of the as-synthesized hollow nanoparticles and the peak positions for Co, Cu and Pt metals. The diffraction peaks could be assigned to a face centred cubic (FCC) phase with a lattice constant of 3.75 Å. This result indicates that the hollow spheres should be in the form of alloy based on Vegard’s law.
CoCuPt hollow nanoparticles

Figure 1. Representative TEM image of Co nanoparticles formed at the early stage of the reaction after the reduction by NaBH4 and prior to the addition of Cu and Pt precursors. Scale bar, 20 nm.

Figure 2. TEM images of as-synthesized porous CoCuPt chain-like hollow structures at (a) low and (b) high magnifications. Scale bars, (a) 20 nm and (b) 2 nm.

(Denton & Ashcroft 1991), because the lattice constant is 3.923 Å for Pt, 3.615 Å for Cu and 3.544 Å for Co. Using the Scherrer equation, we obtained an average domain size of 2.65 nm based on the analysis of the full-width at half-maximum of the (111) diffraction. This value agreed well with the size of crystallites observed in HR-TEM (figure 2b). Our EDX analysis (FE-SEM with the EDAX detector) indicates the average composition of these hollow nanoparticles was Co15Cu32Pt54 (figure 3b). With this chemical composition, the (111) diffraction should be at 0.22 nm according to Vegard’s law. This value agreed well with the data obtained from the XRD study that has the (111) diffraction at 0.223 nm.

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Figure 3. (a) XRD patterns, (b) EDX analysis, (c) HAADF-STEM image and (d) Pt, (e) Cu and (f) Co elemental maps of the as-synthesized hollow nanoparticles.

Figure 4. (a) HAADF-STEM image and (b) its corresponding line scans of Pt, Cu and Co elements of a CoCuPt hollow particle. (a) Scale bar, 20 nm.

Further characterization using STEM and the elemental mapping technique on part of a hollow nanoparticle indicated that all three elements were distributed throughout the particle (figure 3c–f).

EDX line scans were used to further investigate the elemental distribution in hollow nanoparticles (figure 4). All three elements of Pt, Cu and Co were distributed across the spheres. The shapes of EDX line scans for these three
elements were similar and had a flat central region. While detailed spatial distributions of the elements require even higher resolutions, the current results suggest that the signals of these elements are from the wall of a hollow spherical particle.

The formation of CoCuPt hollow nanoparticles thus should most probably follow several major steps based on the experimental observations (figure 5). First, Co$^{2+}$ ions were reduced in the aqueous solution to form Co nanoparticles, which served as the template for the subsequent depositions. Second, the reduced Pt and Cu formed small crystallites that subsequently coalesced to form a shell outer layer. As the shells were composed of tiny grains, soluble ionic species could diffuse across the shell in a counter-diffusive manner (Liang et al. 2004a, b, 2005, 2008; Vasquez et al. 2005). The difference in the diffusion rate of the components at the interface resulted in a net directional flow (Smigelskas & Kirkendall 1947). For this trimetallic system, Co atoms should diffuse faster than those of Pt or Cu to first form core–shell like Co@CuPt hollow nanoparticles, which could be observed in large hollow spheres (Brandes & Brook 1992). As the replacement reaction continued, the net outward movement of Co atoms resulted in the formation of hollow nanostructures of CoCuPt ternary alloys. They formed one-dimensional chain-like nanostructures most probably owing to the strong magnetic dipole–dipole interaction (Thurn-Albrecht et al. 2000). The direction of the chain could be perturbed by the deposition of Cu and Pt atoms. The final morphology of the chain-like hollow nanostructure materials thus was the result of the interactions of the magnetic, steric repulsive and other forces (Puntes et al. 2001; Liang et al. 2004a, 2008; Vasquez et al. 2005).

The as-made hollow nanoparticles were washed extensively with water and ethanol to remove as much PVP as possible. Further calcination in air could be used to get rid of the remaining polymeric capping agent. Figure 6 shows the TGA curves of CoCuPt hollow nanoparticles under both reactive (air) and inert (nitrogen) gases. The major weight loss started at about 100°C and levelled off at about 200°C in air or around 300°C in nitrogen. The oxidation of Co and Cu could result in the taking up of oxygen in the CoCuPt hollow nanoparticles and thus a small overall weight loss when the TGA was carried out under air flow. The removal of PVP in nitrogen seemed to largely complete at about 400°C where about 90 per cent of the total weight loss occurred (figure 6). Thus, in the preparation of hollow catalysts the samples were first treated in air at a predetermined temperature, followed by a reductive annealing process in a forming gas of hydrogen in argon.
As the CoCuPt hollow nanoparticles were prepared at room temperature, grain size was generally small and the crystallinity was also relatively low, as shown in the line broadening in the XRD patterns of as-made particles (figure 7). The XRD pattern shows the as-made hollow nanoparticles had a disordered FCC phase. By annealing the as-made samples at 200°C under a forming gas of 5 percent hydrogen in argon, the XRD line width reduced substantially, suggesting crystallinity was improved and/or the crystalline domain size increased. Further annealing the sample at 400°C resulted in not only the dramatic narrowing of the
CoCuPt hollow nanoparticles

Figure 8. (a–d) TEM and (e–h) HR-TEM images of CoCuPt hollow nanoparticles treated at different temperatures in a forming gas of 5 per cent (v/v) H2 in argon: (a,e) as-made, no treatment, and (b,f) 200, (c,g) 400, and (d,h) 600°C. Scale bars, (a–d) 40 nm and (e–h) 1 nm.

diffraction peak, but also a shift to a higher diffraction angle. The diffractions of the hollow nanoparticles upon annealing at 400°C changed not only in peak intensity and width, but also in 2θ angles. They could be assigned in part to the tetragonal CoPt phase (JCPDS no. 29-0498). Thus, the peak shift to higher 2θ could be due to the incorporation of cobalt and structural change because of the formation of the intermetallic CoPt phase. No further shift in XRD peak position was observed with heat treatment at 600°C, although the line width of the (111) diffraction became quite narrow and resembled that of bulk phase materials, while the diffractions at 48° and 86° split and had shoulder peaks. The characteristic diffractions for the tetragonal phase became obvious, and the peaks at 24.2, 33.4 and 54.4° could be assigned to (001), (100) and (111) planes, respectively. As Co has the smallest lattice parameter (3.54 Å) and served as the sacrificial template, the shift to a high angle suggests that the distribution of the three elements, especially Co, was not even in as-made nanoparticles and further incorporation of Co into the CoCuPt alloy occurred at 400°C. The compositions of all three annealed samples were similar to that of the as-synthesized hollow nanoparticles.

TEM images of the as-made and annealed hollow nanoparticles are shown in figure 8. The overall morphology of chain-like hollow nanostructures was largely intact for those samples treated at 400°C or below (figure 8a–c). We noticed that the size of the crystallites in the walls grew even after annealing at 200°C, while void spaces could still be observed after the heat treatment at this temperature. The difference in the contrast of the TEM images between the wall and interior void regions became more pronounced after the annealing (figure 8c). This observation indicates that uniformity improved substantially after the treatment at 400°C. It seems that this difference was the result of change in composition and incorporation of Co metal. The hollow structures
eventually collapsed and condensed into solid or core-shell solid nanoparticles after annealing at 600°C (figure 8d). HR-TEM study indicates that domain size grew for samples treated with increasing temperature (figure 8e–h). While the as-made nanoparticles had a grain size of about 2 nm, the final solid nanoparticles were typically larger than approximately 20 nm and had a large domain size. The d-spacing of the lattice changed from 2.24 Å for as-made hollow nanoparticles to 2.15 Å for annealed hollow nanoparticles and 2.13 Å for solid nanoparticles, further confirming the incorporation of light-element atoms into the alloys.

The interconnected hollow nanostructures provide a great platform for preparing support-free catalysts. Figure 9a shows a representative nitrogen adsorption–desorption isotherm of the as-made CoCuPt hollow nanoparticles. The Brunauer–Emmett–Teller (BET) surface area obtained from this isotherm was 27.9 ± 0.3 m² g⁻¹ (figure 9b). This value is close to some other nanostructured networks with high specific surface area, but is lower than that of typical 3 nm Pt/C catalysts (Xiong et al. 2004; Gasteiger et al. 2005). As the average grain size in the walls was in the optimal range for Pt/C catalysts to have the best activity for the ORR, it would be interesting to explore the potential of these chain-like hollow nanoparticles as supportless ORR catalysts.

Figure 10 shows the electrochemical properties of four supportless CoCuPt catalysts and a commercial Pt black catalyst (Pt black, HiSPEC 1000, Alfa Aesar) used as the reference. The four CoCuPt catalysts were the as-made hollow nanoparticles and those annealed at 200, 400 and 600°C. The ECSAs of these samples varied from about 40 m² g⁻¹ for the as-made one and that annealed at 200°C to about 27–28 m² g⁻¹ for those samples annealed at 400 and 600°C. The result shows that the as-made and hollow nanoparticles annealed at relatively low temperature had comparable surface areas to those of carbon-supported catalysts. The ECSA value based on the total mass of the metals for the as-made CoCuPt catalyst was 31.6 m² g⁻¹, which is slightly higher than that of the BET surface area. This difference is most probably because the nitrogen molecule cannot diffuse inside the ultrafine porous hollow shells while the proton can diffuse through these pores.
Figure 10. Electrochemical measurements of supportless CoCuPt chain-like hollow structures: (a) CV, (b) hydrodynamic polarization curves, (c) ORR specific activity, and (d) mass activity for as-made sample and samples annealed at 200, 400 and 600°C. The reference catalyst was Pt black. Solid curve, CoCuPt as-synthesized; dot-dashed curve, CoCuPt annealed at 200°C; long-dashed curve, CoCuPt annealed at 400°C; short-dashed curve, CoCuPt annealed at 600°C; dotted curve, Pt black (reference).

Table 1. ORR activity at 0.9 V for supportless CoCuPt nanoparticle electrocatalysts obtained at different annealing temperatures.

<table>
<thead>
<tr>
<th>composition and morphology</th>
<th>$T$ ($^\circ$C)$^a$</th>
<th>Pt loading (µg)</th>
<th>ECSA$^b$ (m² g⁻¹ Pt)</th>
<th>mass activity (A mg⁻¹ Pt)</th>
<th>specific activity (mA cm⁻² Pt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoCuPt, hollow</td>
<td>RT</td>
<td>7.84</td>
<td>40</td>
<td>0.094</td>
<td>0.23</td>
</tr>
<tr>
<td>CoCuPt, hollow</td>
<td>200</td>
<td>7.84</td>
<td>39</td>
<td>0.150</td>
<td>0.37</td>
</tr>
<tr>
<td>CoCuPt, hollow</td>
<td>400</td>
<td>7.84</td>
<td>28</td>
<td>0.072</td>
<td>0.25</td>
</tr>
<tr>
<td>CoCuPt, solid</td>
<td>600</td>
<td>7.84</td>
<td>27</td>
<td>0.050</td>
<td>0.19</td>
</tr>
<tr>
<td>Pt black, solid</td>
<td>RT</td>
<td>20</td>
<td>18</td>
<td>0.029</td>
<td>0.17</td>
</tr>
</tbody>
</table>

$^a$RT stands for room temperature.
$^b$All measurements were made for the 10th CV cycle.

The polarization curves show that as-made CoCuPt and its low-temperature annealed catalysts had more positive on-set potentials than the reference Pt (figure 10b–d and table 1). The CoCuPt hollow nanoparticles annealed at 200°C...
had the highest mass activity of 0.15 A m g⁻¹ at 0.9 V, which was five times higher than that of Pt black (0.029 A m g⁻¹). The specific current density of 200°C-annealed CoCuPt hollow catalyst was 0.37 mA cm⁻². This value was the highest among the samples tested. It was also two times higher than that for Pt black. The as-made and 400°C-annealed CoCuPt hollow catalysts had intermediate activity among these samples, while the solid CoCuPt catalyst was the worst, only slightly better than that of Pt black (table 1). These observations could be explained by the characteristics of the nanostructures, i.e. specific surface area, crystalline structure and composition. Catalysts with a high specific surface area and excellent crystallinity tend to have high activity. Among the three hollow nanoparticles, those annealed 200°C had a high ECSA value and maintained the small domain size, while the as-made sample did not have high crystallinity and the samples annealed at 400°C lost some of the ECSA value and possessed a different chemical composition.

4. Conclusion

Hollow nanostructures of CoCuPt alloys were made by using Co nanoparticles as the sacrificial templates. These hollow nanoparticles can form chain-like nanostructures that have good mechanical strength to be self-supported, and electrical conductivity and chemical composition to be excellent ORR catalysts. It is worthwhile to note that this facile method is based on a room-temperature aqueous phase synthesis and on one of the best-known ternary Pt alloys for catalysing the ORR. Thus, the approach can be regarded as an environmentally benign method for making active electrocatalysts for fuel cell applications. The galvanic replacement reaction using water as solvent is quite suitable for scale-up production because the procedure is simple and carried out under mild ambient room temperature, and has a high yield.

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Phil. Trans. R. Soc. A (2010)
CoCuPt hollow nanoparticles


Phil. Trans. R. Soc. A (2010)


