

Hollow $\text{Sb}_{93}\text{Pt}_7$ Nanospheres Prepared by Galvanic Displacement Reaction for a Highly Li Reactive Material

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Abstract : The synthesis of hollow $\text{Sb}_{93}\text{Pt}_7$ nanospheres smaller than 30 nm with a shell consisting of smaller nanoparticles, with an average particle size of ~3 nm is reported. The formation of this alloy is driven by galvanic replacement reaction involving Sb nanoparticles and H_2PtCl_6 without need for any additional reductants. Further, the reaction proceeds selectively as long as the redox potential between two metals is favorable. The capacities of the hollow samples are 669 and 587 mAh/g at rates of 1 and 7C, respectively, while those values for the nanoparticles are 647 and 480 mAh/g at rates of 1, 7C, respectively. This result shows the significantly improved capacity retention of the hollow sample at higher C rates, indicating that high surface area of the hollow nanospheres makes the current density more effective than that for the solid counterpart.

Keywords : SnPt, Nanosphere, Alloy, Anode, Li storage.

1. Introduction

Lithium reactive metallic nanoparticles have been studied extensively for anode materials in next-generation high capacity Li-ion batteries. In general, the intrinsic properties of metal particles related to volume expansion can be tuned by controlling the size of the particles as well as their structure (core/shell, nanowire).¹⁻⁴⁾ For example, the degree of volume expansion can be reduced by forming core-shell nanoparticles. The volume expansion of $\text{Si}_{90}\text{Sn}_{10}$ with a core size of approximately 15 nm was effectively reduced by a carbon shell with a thickness of approximately 5 nm.²⁾ Many similar investigations of metallic nanoparticles have reported a reduced volume change, which increases the cycle life performance of the electrode materials.⁵⁻¹¹⁾ By processing metal nanoparticles into hollow nanoparticles, performance can be further improved as the empty core can act as a buffer layer to accommodate the volume expansion of the shell to a thickness that is < 5 nm. For instance, mesoporous tin phosphate has been demonstrated as effective in this regard.¹²⁾ It has a reversible capacity with a small amount of capacity fade, while its solid counterpart experiences a loss of its lithium

reactivity of 50% after 30 cycles. Furthermore, the hollow nanoparticles is expected to greatly improve the rate capability at higher current rates compared to the solid counterparts as the hollow nanoparticles have larger electrolyte and electrode contact areas compared to their solid counterparts.

Hollow nanostructures consisting of metals are often fabricated by depositing thin layers of metals (or their precursors) on existing templates, such as silica and polymers, followed by firing or wet chemical etching to remove the core.¹³⁻¹⁷⁾ On the other hand, Sun et al. reported a one-step approach based upon galvanic replacement reaction that was capable of generating hollow nanostructures consisting of Au, Pd, and Pt.¹⁸⁾ This method employs a sacrificial nanoparticle in which a galvanic replacement reaction with another suitable metal ion results in the formation of excellent hollow particles that take the morphology of the sacrificial partner. Although bimetallic AuPt ¹⁹⁾, CoPt ²⁰⁾, and NiPt ²¹⁾, AuAg ²²⁾ nanoparticles have been investigated, no studies on lithium reactive hollow bimetallic nanoparticles have been reported.

This study demonstrates that a similar galvanic replacement reaction involving Sb nanoparticles and H_2PtCl_6 results in hollow $\text{Sb}_{93}\text{Pt}_7$ nanoparticles for lithium battery anode material for the first time.

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The bimetallic hollow nanoparticles demonstrate low polarization and significantly improved capacity retention at a higher current compared to its solid counterpart.

2. Experimental Section

Hollow $\text{Sb}_{93}\text{Pt}_7$ (at%) nanospheres were prepared using a modified procedure reported by Vasquez et al.²⁰ In a typical synthesis, 1.4 g of $\text{SbCl}_3 \cdot 6\text{H}_2\text{O}$ (99%, Aldrich) and 1 g of PVP (Mw = 55,000, Aldrich) were dissolved in 300 ml of deionized water for 30 min. with purging with purified Ar gas. On the other hand, 10 g of NaBH_4 (99%, Aldrich) dissolved 100 mg of deionized water was slowly injected into the stirring mixture solution of $\text{SbCl}_3 \cdot 6\text{H}_2\text{O}$ and PVP that using a syringe. After all the NaBH_4 was added, 0.97 g of H_2PtCl_6 (99.9%, Alrich) dissolved in 40 ml H_2O was added dropwise with stirring, and the mixture was refluxed for

5 min. The product was then collected by centrifugation, washed 6 times with purified water, ethanol, and dried at 21°C under vacuum for overnight.

XRD patterns were obtained using a $\text{Cu K}\alpha$ X-source on a Rigaku instrument operated at 11 kW. HRTEM samples were prepared by the evaporation of the dispersed nanoparticles in acetone or hexane on carbon-coated copper grids. Transmission electron microscope (TEM) and high resolution TEM (HRTEM) analysis were performed on JOEL 2100F, and field scanning electron microscope (FE-SEM) images were taken on Philips XL-30 equipped with an energy dispersive x-ray (EDX) spectrometer. The electrodes for the battery test cells were made of active material, super P carbon black, and polyvinylidene fluoride (PVDF) binder (Solef) in a weight ratio of 8 : 1 : 1. The slurry was prepared by thoroughly mixing a *N*-methyl-2-pyrrolidone (NMP) (Aldrich) solution of PVDF, carbon black, and the anode

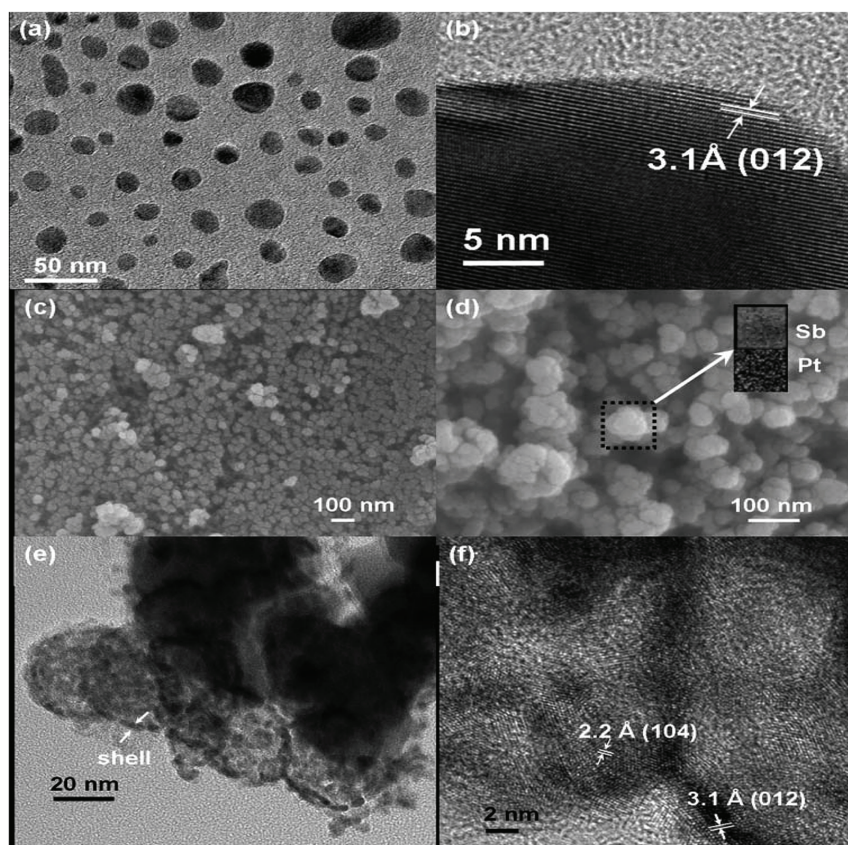


Fig. 1. (a) TEM images of the Sb nanoparticle templates and (b) HRTEM image of (a), (c and d) low and high magnification of SEM images of hollow $\text{Sb}_{93}\text{Pt}_7$ nanospheres prepared using Sb nanoparticle templates and (d) elemental mapping of Sb and Pt for the sphere in (d), (e and f) TEM images of the hollow $\text{Sb}_{93}\text{Pt}_7$ nanospheres.

material. The coin-type half cells (2016R size), prepared in a helium-filled glove box, contained a active material, a Li metal anode, a microporous polyethylene separator, and an electrolyte solution of 1.05 M LiPF₆ in ethylene carbonate/dimethyl carbonate (EC/DMC) (1 : 1 vol%) (Cheil Industries, Korea).

3. Results and Discussion

Fig. 1a and b show TEM images of Sb nanoparticles obtained after an addition of NaBH₄ to a solution of Sb³⁺ and PVP. These dense spheres with an average particle size of approximately 25 nm provide an in situ template for the formation of hollow SbPt spheres on the basis of the following reaction: $\text{Sb}^{3+} + \text{PtCl}_6^{2-} = \text{Pt} + \text{Sb}^{3+} + 6\text{Cl}^-$. To avoid the oxidation of Sb nanoparticles, Ar is bubbled through the solution during the entire procedure. HREM image b clearly shows the presence of the lattice fringe of the (012) plane, corresponding to a Sb *d*-spacing value of 3.1 Å. After the addition of Pt⁴⁺ into the solution with the Sb nanoparticles, SEM images (c and d) show the presence of the aggregated nanoparticles composed of individual particles that are < 30 nm. Here, the elemental mapping of the single particles confirms the uniform distribution of Sb and Pt atoms (inset of image d).

In addition, the TEM image (e) shows that the centers of the spheres are brighter than the edges, indicating that individual SbPt spheres are composed of an empty core with a shell; to be precise, this shows that a hollow structure exists. Moreover, the image shows that the shell consists of smaller nanoparticles, with an average particle size of ~3 nm. The shell of the SbPt hollow nanospheres is rough and appears incomplete and porous. Similar morphology was also observed in CoPt²²⁾ and Pt.²³⁾ The thickness of the shell is approximately 3 nm and the average diameter of the nanospheres is approximately 25 nm. HREM image f clearly shows the presence of the lattice fringe of the (104) and (012) planes, corresponding to a Sb *d*-spacing value of 2.2 Å and 3.1 Å, respectively. The measured BET surface area of the hollow sample was 65 m²/g while that of the nanoparticle Sb was 37 m²/g.

As the standard reduction potential of the Pt⁴⁺/Pt redox pair ($E^0 = 0.735$ V vs. SHE) is much higher than Sb³⁺/Sb ($E^0 = 0.15$ V vs. SHE), Sb nanoparticles are oxidized to Sb ions when the Sb nanoparticle solution is added to the H₂PtCl₆ solution. However, in terms of the reduction potential, Sb is much higher than Co²⁺/Co

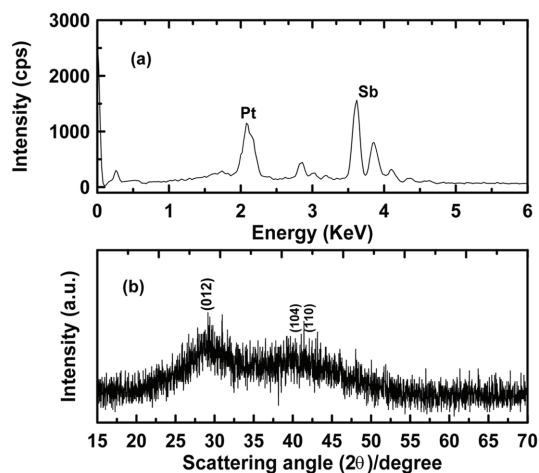


Fig. 2. EDX and XRD patterns of the hollow Sb₉₃Pt₇ nanospheres.

($E^0 = -0.277$ V vs SHE), and the galvanic replacement reaction rate is expected to be slower than that of Co in MPt (M = Sb or Co). Hence, the Pt⁴⁺ that was added was not fully incorporated into the reaction with Sb. However, hollow Co₅₈Pt₄₂ nanoparticles were formed as soon as the H₂PtCl₆ was injected into the aqueous solution containing Co nanoparticles (about 1 min). As proposed by Vasquez et al.,²²⁾ due to the excess BH₄⁻ in the reaction flask, any Sb that is oxidized to Sb³⁺ during Pt deposition will be reduced back to Sb. As PVP is known to bind metal cations,¹⁸⁾ it can trap the liberated Sb³⁺ ions and Pt⁺ simultaneously. It will then co-reduce near the surface of the nanospheres.

Energy-dispersive X-ray spectroscopy (Fig. 2a) does not show a peak of oxygen at 0.4eV and confirms the stoichiometry of Sb₉₃Pt₇, indicating that the as-prepared sample was not oxidized. Powder X-ray diffraction of the Sb₉₃Pt₇ (Fig. 2b) is indexed to a single phase rhombohedral structure with a R-3m space group. The existence of relatively broad diffraction peaks is consistent with the nanocrystalline nature of the shell, and average particle size of 2.6 nm is in good agreement with the TEM results. Although the Pt is an FCC structure, the single phase formation indicates that Pt atoms are completely incorporated into the Sb lattices. In nanoscale materials, supersaturated alloys can be formed without phase segregation, for example, 10 at% Ni with a FCC structure²⁴⁾ or 10 at% Co atoms with a HCP structure²⁵⁾ can supersaturated into tetragonal tin. Similarly, in a macroporous Sn-Co alloy, over 40 at% Co was reported to be supersaturated in Sn lattices.²⁶⁾

Figs. 3a and b show the voltage profiles of the hollow $\text{Sb}_{93}\text{Pt}_7$ and nanoparticle Sb in coin-type half cells between 0 and 1.5 V at 0.2, 1, 5, and 7C rates (1C = 600 mA/g). The cells contained 20~25 mg/cm² of the active material. The coulombic efficiency of the hollow sample (68%) is lower than that of the nanoparticle sample (72%), indicating that the higher BET surface area contributes to an increased irreversible capacity during the first cycle. Relatively large first discharge capacity (~1,000 mAh/g) is due to the formation of the solid electrolyte interface (SEI) and more lithium reaction sites associated with the nanosize effect.

The capacities of the hollow samples are 669, 643, and 587 mAh/g at rates of 1, 5, and 7C, respectively, while those values for the nanoparticles are 647, 611, and 480 mAh/g at rates of 1, 5, and 7C, respectively; this shows the significantly improved capacity retention of the hollow sample at higher C rates. In addition, the plateau voltage of the nanoparticles increases as the current rate increases, in contrast to that of the hollow sample, indicating the increased interfacial polarization between the electrode and the electrolyte as the current increases in the nanoparticle electrode. Fig. 3c compares

the cycle life performance of the hollow and nanoparticle samples, showing that the charge capacities of Sb nanoparticles, at 3 and 7C decrease rapidly, in contrast to the hollow $\text{Sb}_{93}\text{Pt}_7$. The figure also shows that the capacities of the hollow and nanoparticle samples are 580 and 400 mAh/g, respectively, after 5 cycles at a rate of 7C. The improved capacity retention of the hollow sample compared to that of the Sb nanoparticle is a result of the electrolyte-enhanced contact area of the hollow nanoparticles, which provided enhanced electronic and Li ion conductivity. However, it should be noted that the excellent capacity retention properties of the hollow sample are also related to the fact that the ~3nm nanoparticles consisting of hollow particles undergo a reversible volume change without aggregation into larger Sb clusters during cycling. It has been reported that the critical particle size for reversible volume change during lithium alloy and dealloy procedures is approximately 3 nm.²⁷⁾

4. Conclusions

Hollow $\text{Sb}_{97}\text{Pt}_3$ nanoparticles were successfully prepared via a galvanic replacement reaction. The diameter and shell sizes of the as-prepared the nanoparticles were nearly 25 and 3 nm, respectively. As porous empty cores were created in the cores of dense Sb nanoparticles during a replacement reaction with Pt, the electrochemical performances at higher C rates were significantly improved by more than 40% compared to the $\text{Sb}_{97}\text{Pt}_3$ nanoparticles. Because of the formation of the empty core, the volumetric energy density of the cell is expected to be decreased, compared to its solid counterpart. However, hollow metallic $\text{Sb}_{97}\text{Pt}_3$ anode demonstrated higher energy density than its solid counterpart at higher current rates.

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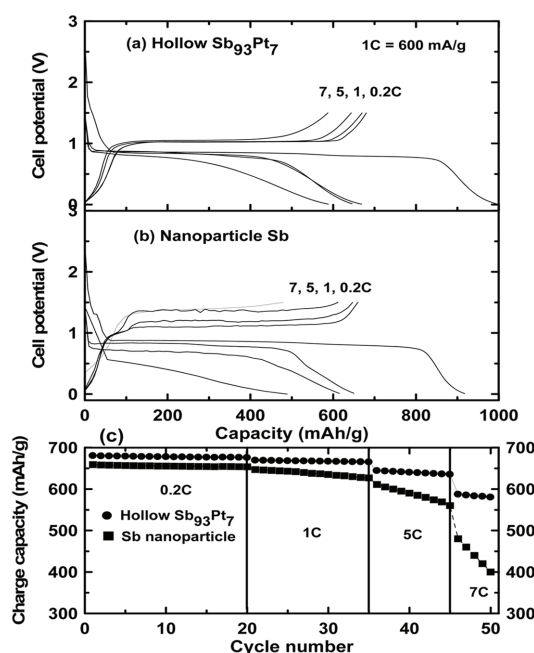


Fig. 3. (a and b) Voltage profiles of the Sb nanoparticles and hollow $\text{Sb}_{93}\text{Pt}_7$ nanospheres at different C rates between 0 and 1.2 V in coin-type half cells. (c) Charge capacities vs. cycle number at different C rates.

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