

Ag Nanowires Coated with Ag/Pd Alloy Sheaths and Their Use as Substrates for Reversible Absorption and Desorption of Hydrogen

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Studies on the interaction between metals and hydrogen have become increasingly important as driven by the need to develop hydrogen absorption materials with optimal properties in terms of hydriding/dehydriding kinetics, hydrogen-uptake capacity, cycle stability, as well as reasonable production costs.¹ Pd-based alloys offer a class of attractive materials for studying metal hydrides because of higher solubility and permeability of hydrogen in such alloys than in pure Pd.² For example, Pd/Ag alloy, the most commonly used material for hydrogen extraction in industry, has been demonstrated to exhibit the highest permeability for hydrogen at ~23 wt % of Ag when measured at a pressure of 1 atm and temperature above 473 K.^{3,4} It has also been shown by simulation that a further increase of Ag to higher concentrations (>63%) could lead to faster diffusion for hydrogen (as well as to lower the material cost).⁵ Furthermore, it has long been speculated that, when the grains of metals are reduced to the nanometer regime, they may exhibit significant improvement in hydrogen absorption behaviors due to an increase in surface area and grain boundaries. Here we demonstrate that Ag nanowires could exceed pure Pd powders or nanotubes in hydrogen solubility when the surfaces of such wires were coated with thin sheaths of Pd/Ag alloys (with the total percentage of Ag in the system as high as 92.2 wt %).

The silver nanowires were synthesized using a modified polyol method⁶ and were then refluxed with Pd(NO₃)₂ in an aqueous solution for 30 min. In contrast to our previous demonstration that the short Ag nanowires (e.g., <2 μm in length) yielded Pd nanotubes through the galvanic replacement reaction,⁷ here we found that only some segments of the nanowires were converted into hollow structures when their lengths were increased up to 20 μm. Such a difference in morphology could be attributed to the fact that Pd²⁺ might have lost its reactivity (due to hydrolysis) before the entire Ag wire had been transformed into a tubular entity. Although the dissolution of Ag was inhomogeneous across the surface of a nanowire, the resultant Pd atoms were homogeneously deposited on the surface of each wire.⁸ As it was shown by Sastry et al., Ag and Pd tended to form alloys when Ag@Pd core-shell colloids were annealed at 100 °C.⁹ Since our reaction was conducted at 100 °C also, we believed that Pd atoms resulting from the galvanic reaction also formed alloys with Ag atoms on the surface of each nanowire. On the basis of this argument, the surface of each Ag wire should be coated with a conformal, thin sheath of Pd/Ag alloys to form a cable-like structure.

Panels A and B of Figure 1 show the SEM images of a typical sample, where Ag wires of ~60 nm in diameter were coated with Pd/Ag sheaths and then subjected to sonication for 5 min. Note that each nanowire was straight and uniform in diameter along the entire long axis. Due to sonication, some wires were broken at the sites with hollow interiors, indicating that the formation of tubular

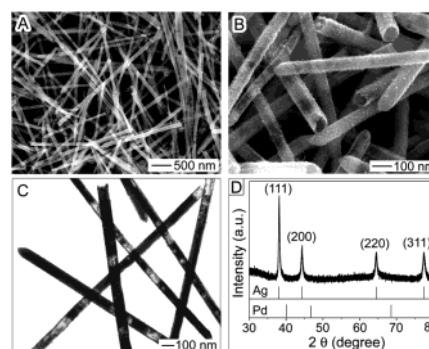


Figure 1. (A, B) SEM images, (C) TEM image, and (D) XRD pattern of Ag nanowires whose surfaces had been coated with Pd/Ag alloy sheaths.

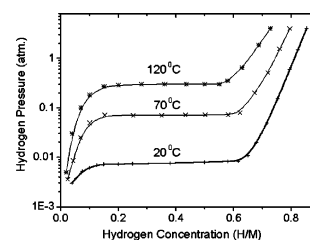


Figure 2. PC isotherms for hydrogen desorption from the hydrides of as-synthesized Ag@Pd/Ag nanocables at 20, 70, and 120 °C. Here H/M is the hydrogen-to-metal ratio.

segments decreased the mechanical strength of these wires. It is also clear from Figure 1B that the surfaces of these Ag wires were decorated with many small particles having lateral dimensions of 3–10 nm. The surface roughness could be ascribed to the poor epitaxial growth of Pd on Ag as caused by the relatively large difference (~4.8%) in lattice constant between Ag and Pd. The composition of the final product was analyzed by atomic emission spectrometry, indicating that it was composed of Ag and Pd with 92.2 and 7.8 in weight percentage, respectively. Figure 1C shows a TEM image of this sample, confirming the existence of hollow segments (the replacement reaction should be initiated from these sites^{8b}) with a total volume fraction of ~10%. The XRD pattern shown in Figure 1D indicates that this product was in the face-centered cubic phase with a lattice constant (4.07 Å) very close to that of pure Ag ($a = 4.086 \text{ \AA}$, JCPDS File 04-0783). This result implies that the crystalline lattice of Pd/Ag alloy sheaths was also dominated by the framework of Ag. This observation agreed with the STM and Auger electron spectroscopic (AES) studies, where Ag atoms were found to have a strong tendency to diffuse from bulk to surface when they were alloyed with Pd.¹⁰

The thermodynamic aspects of metal–hydrogen interactions are usually understood from pressure-composition (PC) isotherms.¹¹ Figure 2 shows the PC isotherms of an as-synthesized sample (without sonication) at 20, 70, and 120 °C. It is worth noting that distinct plateaus were formed similar to those of polycrystalline

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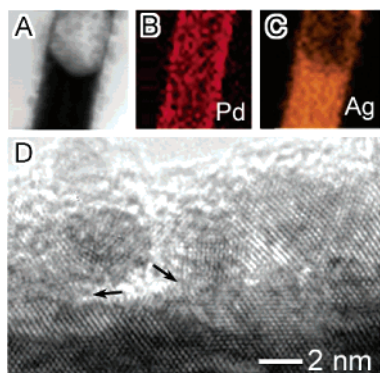


Figure 3. (A) TEM and (B, C) EDX elemental mapping of an as-obtained Ag@Pd/Ag nanocable. (D) High-resolution TEM image taken from the edge of such a nanostructure.

Pd powders of ~ 3 nm in size (Figure S1, Supporting Information), indicating the existence of a broad metal–H miscibility gap for the Pd/Ag-coated Ag wires. More specifically, the hydrogen solubilities (at 20 °C) at α -($\alpha + \beta$) and $(\alpha + \beta)$ - β phase boundaries were respectively 0.11 and 0.64 in terms of atomic ratio between hydrogen and metal for the nanocables and 0.008 and 0.61 for the Pd powders.¹² The higher concentration of hydrogen at the α -($\alpha + \beta$) boundary for the nanocables was caused by smaller sizes (< 10 nm) of Pd/Ag alloyed nanoparticles formed on the surface of each Ag nanowire.¹³ As the temperature was decreased, the content of absorbed hydrogen was increased, accompanied by broadening of the miscibility gap. According to the Van't Hoff equation, the changes in enthalpy (ΔH) and entropy (ΔS) associated with hydrogen desorption from the Ag@Pd/Ag nanocables were calculated as 35.95 kJ/mol and 81.51 J/K·mol, respectively, which were close to those of Pd powders (38.87–40.96 kJ/mol for ΔH , and 91.96 J/K·mol for ΔS).¹⁴ It is worth pointing out that the absorption and desorption of hydrogen were reversible and the reactions at room temperature were very fast for the present system. For instance, the desorption process could be completed in about 10 min at 20 °C.

The high solubility of hydrogen in the nanocable structures can be attributed to the formation of a thin sheath of Pd/Ag alloy nanoparticles on the surface of each Ag wire because hydrogen is not soluble in pure silver.¹⁵ The distribution of Ag and Pd across the surface of an individual wire was examined by EDX mapping. Panels A–C of Figure 3 show some results taken from the region of a cable that contained both solid and hollow segments. It is clear that the wall of the hollow portion and the surface of the solid portion contained both Pd and Ag. In comparison, the center of solid segment was mainly filled with Ag. The Pd/Ag alloy sheaths can decompose H₂ molecules into H atoms with high efficiency due to its relatively larger lattice constants than those of pure Pd.¹⁶ The morphology and structure of their surface were further studied using high-resolution TEM, and a typical image is shown in Figure 3D. It is clear that all the small nanoparticles were crystallized and sintered on the surface of each Ag wire to form necks (as indicated by arrows) due to the relatively high temperature (100 °C) involved in the synthesis. These necks provided an effective route for the diffusion of H-atoms from the surface into the lattice of Ag nanowire. The diffusion of H atoms in the Ag lattice might be easier than in pure Pd or a Pd/Ag alloy because the relatively larger lattice constant of Ag could facilitate the transportation process.⁵ In this proposed model, the Pd/Ag alloy sheath acts as a catalyst to dissociate H₂ into H in the process of absorption, and served as a “hydrogen pump” to aid the complete decomposition of hydride in the process of desorption.¹⁷

To determine if the formation of hollow segments contributed significantly to hydrogen absorption, the PC isotherms (Figure S2) of pure Pd nanotubes (synthesized by templating against alumina membranes¹⁸) were also measured. These nanostructures exhibited capacities similar to those of the Ag/Pd-coated Ag nanowires in hydrogen absorption, indicating that the mechanism of hydrogen absorption in these nanostructures is determined by the formation of hydride rather than the physisorption and/or capillary effects associated with the tubular morphology. In addition, we found that the Ag@Pd/Ag nanocables had greatly improved mechanical strength in the formation and decomposition of metal hydrides as only minor volume expansion and shrinkage were involved. For example, the nanocables were only slightly bent or broken at some locations next to the hollow segments after 50 cycles of hydrogen absorption and desorption, while the pure Pd nanotubes collapsed into particles only after 25 cycles (see Figure S3 for TEM images). Further studies on the kinetics of hydrogen absorption and desorption should enable us to achieve a better understanding of the hydriding/dehydriding processes, as well as to develop cost-effective, safer materials for related applications.

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Supporting Information Available: Procedures for preparing the metal nanostructures and measuring the PC isotherms, PC isotherms for Pd powders and nanotubes, and TEM images of the core-sheath nanowires or Pd nanotubes after 50 or 25 cycles of hydriding and dehydriding. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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