Electronic Supplementary Information for:

An ultrafine nanoporous bimetallic Ag-Pd alloy with superior catalytic activity

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Experimental procedure:

The alloy with nominal composition of $Mg_{65}Ag_{28}Pd_7$ was prepared from pure Mg (99.9 wt.%), pure Ag (99.95 wt.%) and pure Pd (99.9 wt.%) in a quartz crucible using a high-frequency induction furnace in an argon atmosphere. Using a single roller melt spinning apparatus, the pre-alloyed ingots were remelted in a quartz tube by high-frequency induction heating and then melt-spun onto a copper roller at a circumferential speed of ~ 18 $m \cdot s^{-1}$. The ribbons obtained were normally 30 μm in thickness, 2 mm in width and several centimeters in length. During the melting and remelting process, loss of Mg occurred due to volatilization, oxidation and burning of active Mg. The actual composition of the melt-spun ribbons was determined to be 59.9 at.% Mg, 32.0 at.% Ag and 8.1 at.% Pd by energy dispersive X-ray (EDX) analysis. In this communication, the actual composition was used and designated as $Mg_{60}Ag_{32}Pd_8$ for simplicity.

The rapidly solidified $Mg_{60}Ag_{32}Pd_8$ ribbons were dealloyed in a 5 wt% HCl aqueous solution under free corrosion conditions. The dealloying was first performed at room temperature until no obvious bubbles emerged. Then the dealloying was continuously carried out at 90 ± 5 ºC to further leach out the residual Mg. The typical dealloying time was 35 min. After dealloying, the nanoporous Ag-Pd alloy with a nominal composition of $Ag_{80}Pd_{20}$, was rinsed using distilled water and dipped in distilled water for 24 hours to avoid the spontaneous combustion of Pd. Nanoporous Pd was fabricated by dealloying of $Al_{80}Pd_{20}$ ribbons which were also prepared by the melt spinning technique. The dealloying was performed in a 20 wt% NaOH aqueous solution under free conditions. The detailed synthesis procedure of nanoporous Pd can be found elsewhere.[20] (Z. H. Zhang, Y. Wang, Z. Qi, W. H. Zhang, J. Y. Qin and J. Frenzel, *J. Phys. Chem. C*, 2009**, 113**, 12629.)

Microstructural characterization of the rapidly solidified $Mg_{60}Ag_{32}Pd_8$ alloy and the as-dealloyed samples was performed using X-ray diffraction (XRD, Hitachi Rigaku D/max-RB), scanning electron microscopy (SEM, LEO 1530VP), energy dispersive X-ray (EDX) analysis, transmission electron microscopy (TEM, Philips CM20) with selected-area electron diffraction (SAED), and high resolution transmission electron microscopy (HRTEM, FEI Tecnai G2). For EDX analysis, at least five measurements were performed and an average value was presented in the communication. In addition, the HCl solution after dealloying was examined by inductively coupled plasma (ICP, IRIS Advantage) apparatus to detect the minor dissolution of Ag during dealloying.

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Electrochemical measurements:

Electrochemical measurements were performed in a standard three-electrode cell using a LK 2500A Potentiostat. The nanoporous $Ag_{80}Pd_{20}$ electrode was prepared as follows: 4 mg nanoporous $Ag_{80}Pd_{20}$, 4 mg carbon powders, 300 μL isopropanol and 100 μL Nafion solution (0.5wt.%) were ultrasonically mixed for 90 min. About 5 μL of the mixed suspension was dropped on a freshly polished glassy carbon (GC) electrode with a diameter of 4 mm. The electrode was used as the working electrode. The counter electrode was a Pt plate, while a Hg/HgO electrode (MMO) or a saturated calomel electrode (SCE) was used as the reference electrode. Prior to electrochemical measurements, the electrolytes were deoxygenated by bubbling with N_2 for 10 min. The electrochemically active surface area (EASA) of each electrode was calculated by the oxygen adsorption method.[27] (S. Trasatti, O. A. Petrii, *Pure Appl. Chem.* 1991, **63**, 711.) Cyclic voltammogram (CV) measurements were performed in a 1M H_2SO_4 solution. By integration of symmetrical cathodic peaks resulting from electrochemical reduction of Pd oxide monolayer that formed in the previous anodic scan (see Fig. E4), the amounts of reduction charge were determined to be ~13.04 and 10.84 mC for the nanoporous $Ag_{80}Pd_{20}$ and nanoporous Pd electrodes respectively. The EASA of nanoporous $Ag_{80}Pd_{20}$ and nanoporous Pd was therefore determined to be ~ 30.74 and 25.56 cm^2 by dividing the amount of reduction charge by palladium's conversion factor of 424 $\mu C\ cm^{-2}$. [27] The voltammetric behavior of both electrodes was characterized in a 1M KOH solution. Catalytic activity was measured in a solution of 1M KOH + 1M ethanol. All electrochemical experiments were performed at room temperature with a scan rate of 50 mV s^{-1}.

Figures:

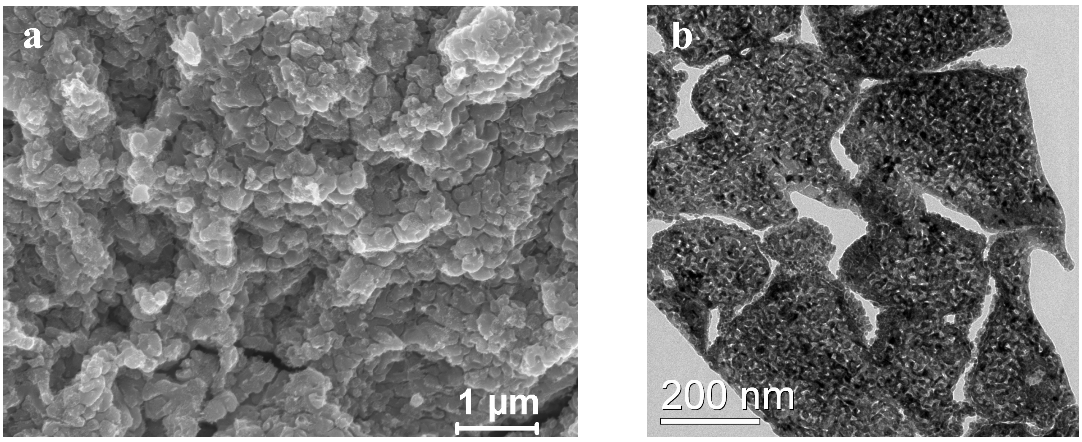

Fig. E1 (a) SEM and (b) TEM micrographs showing the microstructure of the nanoporous $Ag_{80}Pd_{20}$ alloy by dealloying the rapidly solidified $Mg_{60}Ag_{32}Pd_{8}$ alloy in the 5 wt.% HCl aqueous solution.

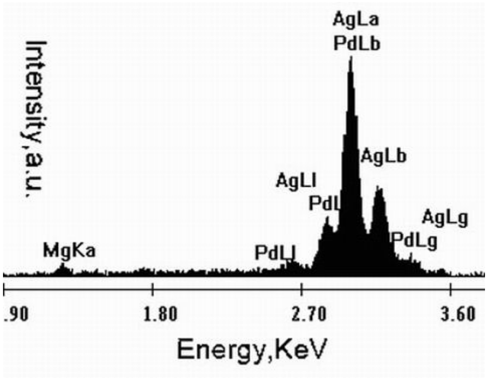

Fig. E2 EDX spectrum of the as-dealloyed sample.

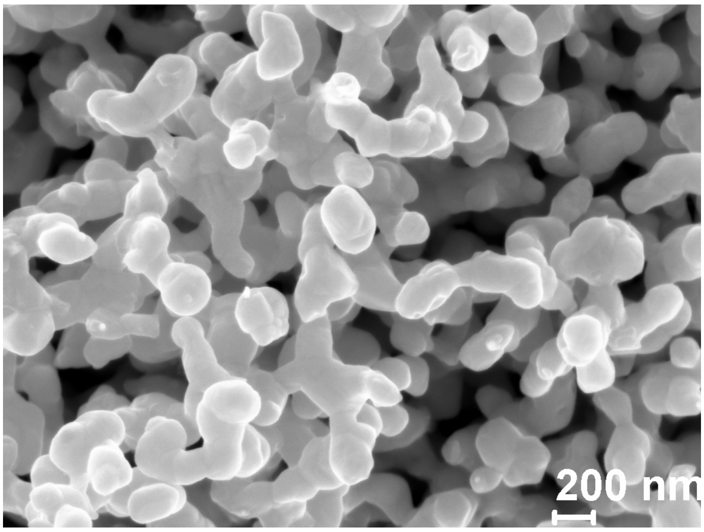

Fig. E3 SEM micrograph showing the microstructure of nanoporous Ag by dealloying the melt-spun $Mg_{65}Ag_{35}$ alloy in the 5 wt.% HCl aqueous solution.

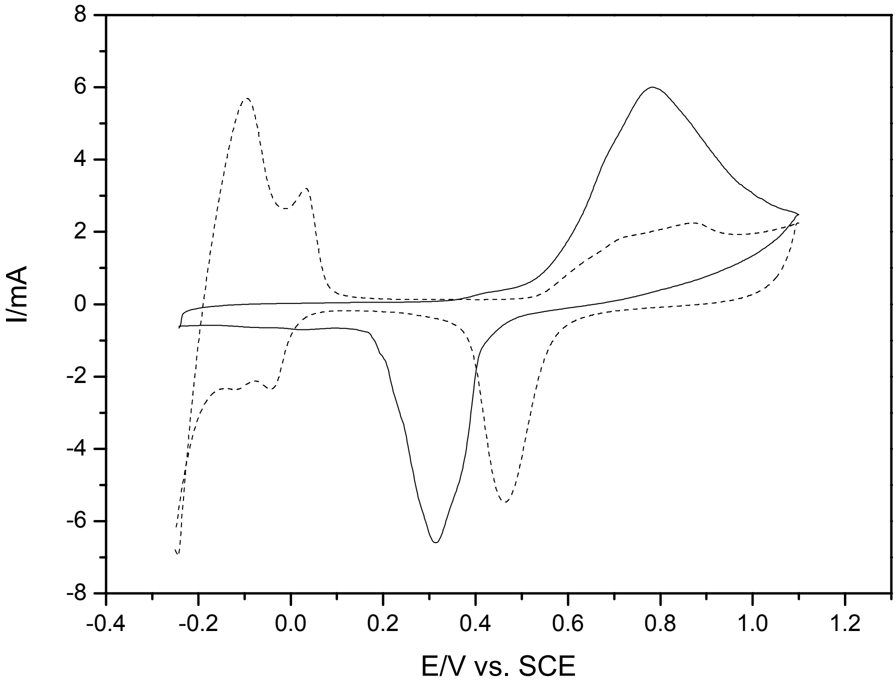

Fig. E4 CVs for the nanoporous $Ag_{80}Pd_{20}$ electrode (solid line) and the nanoporous Pd electrode (dash line) in the 1M H_2SO_4 solution. Scan rate: 50 mV s^{-1}.

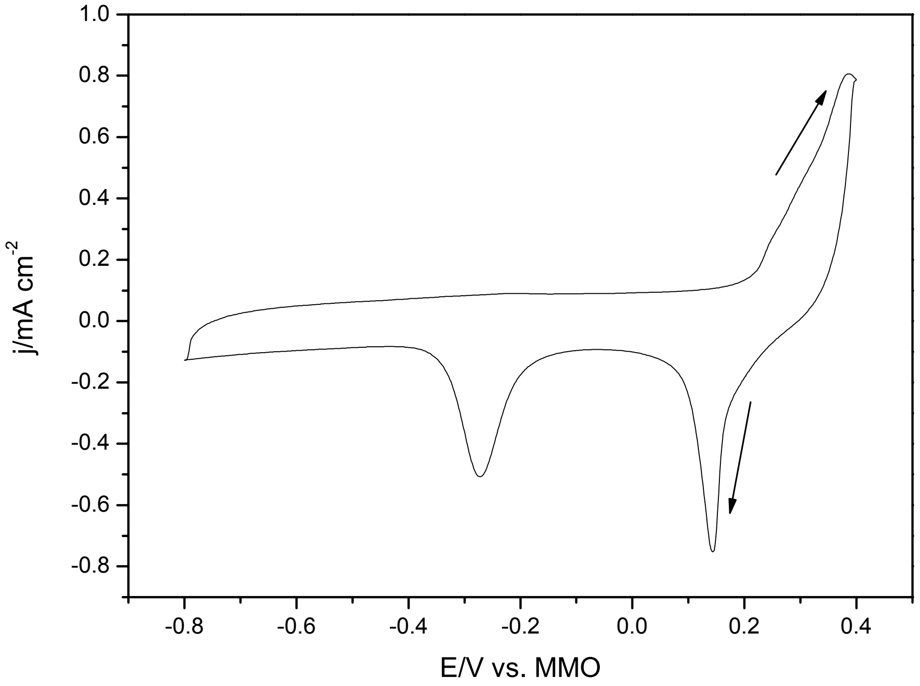

Fig. E5 CV for the nanoporous $Ag_{80}Pd_{20}$ electrode in the 1 M KOH solution. Scan rate: 50 mV s^{-1}.