Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Porous platinum nanowire arrays for direct ethanol fuel cell applications

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Experimental

Nanochannel alumina templates are prepared by anodizing high purity aluminum foils (99.999%) in acid solutions using a two-step anodization method.[1,2] Alumina templates with thickness of 6 μm and pore diameter of about 60 nm were used to synthesize Pt and Pt-Cu nanowires. We chose Pt-Cu alloy system because the Pt-Cu system is capable of forming continuous series of solid solutions, and a homogeneous Pt-Cu alloy has a predictable and consistent microstructure. In order to electrodeposit Pt and Pt-Cu alloy, Au thin film with thickness about 100 nm was deposited on one side of the anodic porous alumina template as electrode by using vacuum evaporation apparatus. Pt-Cu alloy nanowires were deposited from a 0.5M H_2SO_4 solution containing 5g/liter H_2PtCl_4 and 12g/liter $CuSO_4$ by using a galvanostatic method. Pt/Pt-Cu heterojunction nanowires were fabricated by using a two-step electrodeposition method: First, Pt nanowires were deposited from a 0.5M H_2SO_4 solution containing 5g/liter H_2PtCl_4. Then Pt-Cu alloy nanowires were deposited under the same condition as mentioned above. Unless otherwise noted, the electrodeposition was carried out at a current density of 400μA/cm^2. After electrodeposition, a layer of silver epoxy was coated on the back side of the Pt-Cu loaded template to reinforce the nanowire arrays. The template was etched away by using 5wt. % phosphoric acid to release the nanowire arrays. Pt-Cu alloy nanowires maintain their positions after carefully removal of alumina because they are restricted and supported by the substrate. Then the alloy sections of the nanowires were dealloyed with the removal copper component by using 20 wt.% nitric acid solution. The

main purpose of fabrication of Pt/Pt-Cu heterostructure nanowires is to assure the roots of the nanowires unchanged and retain the order of the nanowire array during the dealloying process. Besides, the Pt/Pt-Cu heterostructure make it convenient to observe the change of the nanowire diameter after the removal of copper component. All electrochemical deposition and electrochemical measurement were carried out on an electroanalytical instrument (autolab II) at room temperature. The Pt nanowire array with about 2 μm of porous Pt segment and 200 nm of Pt end segment prepared by the etching of Pt/ $Pt_{0.28}Cu_{0.72}$ nanowires and a solid Pt nanowire array with 2.2 μm length deposited at 400 μAcm^{-2} were prepared. The obtained Pt nanowire arrays were cleaned by distilled water, and ethanol and dried. Then the Pt nanowire arrays were mounted on a circle copper electrode and inserted into the electrochemical cell as working electrodes, and a circular area (5 mm diameter) was exposed to the electrolyte. A Pt film electrode was prepared by electrodepositing Pt on a glassy carbon electrode under the same condition as for the Pt nanowire array for comparison. The KCl saturated Ag/AgCl electrode was used as a reference electrode, and a Pt wire was used as a counter electrode. The morphology, composition, and microstructure of the Pt-Cu and porous Pt nanowires were investigated by using a scanning electron microscope (SEM, JEOL JSM-6300F) with energy dispersive X-ray spectroscopy (EDS) and a transmission electron microscope (TEM, CM20) operated at 200 KV.

References:

1. H. Masuda, and K. Fukuda, *Science* 1995, **268**, 1466-1468.
2. H. Masuda, and M. Satoh, *Jpn. J. Appl. Phys. Part 2* 1996, **35**, L126-L129.

Table S1

Electrode	Pt loading ($mgcm^{-2}$)	Q_H ($mCcm^{-2}$)	S_{EAS} (cm^2mg^{-1})	S_{EASS} (cm^2cm^{-2})
Pt PNWA	0.79	21.7	130.1	103.3
Pt NWA	2.4	18.4	36.6	87.8
Pt film	4.7	4.3	4.36	20.4

[a]$Q_{H:}$ charges exchanged during the electroadsorption of hydrogen on Pt
[b]S_{EAS}: electrochemical active surface area, $S_{EAS} = Q_H/0.21L_{Pt}$, where the L_{Pt} is the Pt loading and 0.21 is the charge required to oxidize a monolayer of H_2 on smooth Pt ($mCcm^{-2}$).
[c]S_{EASS}:electrochemical active specific surface area, $S_{EASS} = Q_H/0.21A_G$, where A_G is the geometric area of the electrode.

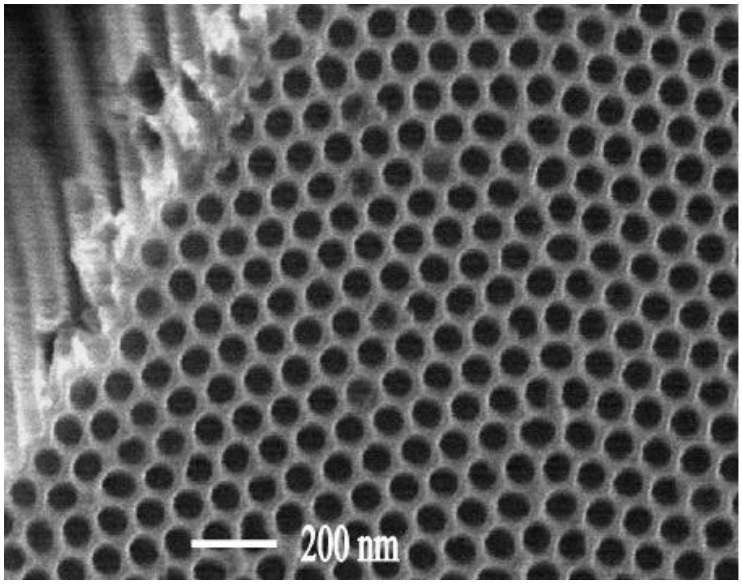

Figure S1. SEM image of hexagonal close-packed arrays of nanochannel alumina template with 60 nm pore diameter.

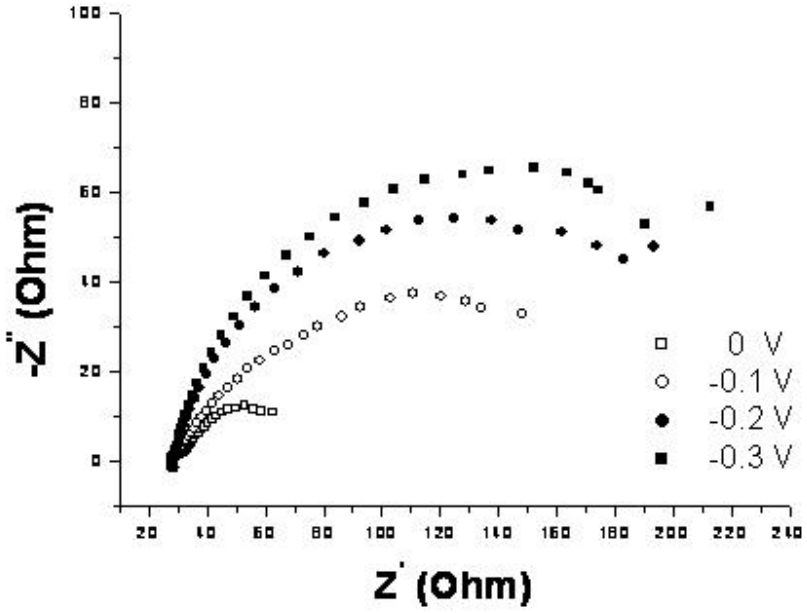

Figure S2. Nyquist plot for ethanol oxidation on the porous Pt nanowire array electrode at different potential in 1 M NaOH + 1 M ethanol.

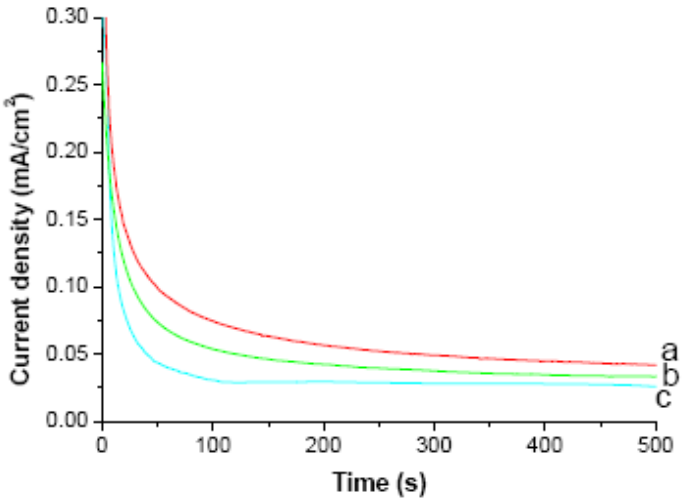

Figure S3. Chronoamperometric curves for ethanol oxidation in 1 M NaOH + 1 M ethanol at 0.1 V on (a) Porous Pt nanowire array electrode; (b) Pt nanowire array electrode; (c). Pt film electrode. The current densities are normalized to the electrochemically active surface area.