Facile synthesis of continuous Pt island networks and their electrochemical properties for methanol electrooxidation†

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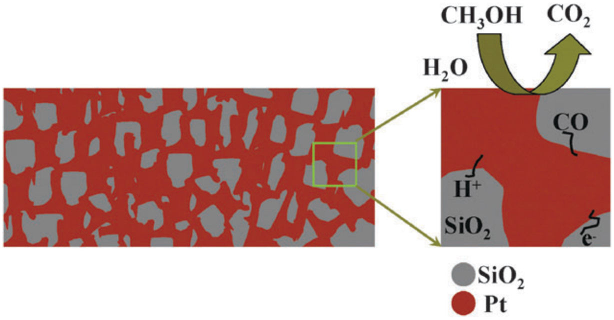
A two-dimensional continuous Pt island network was successfully synthesized by pulse-potentiostatic electrodeposition on a flat silicon substrate, which showed markedly enhanced catalytic activity toward methanol electrooxidation and high CO tolerance, probably due to the synergistic effect of the Pt island catalyst and surrounding SiO_2 surface layer.

Over the past few years, synthesis of nanostructured materials has received great interest in the technology due to its wide range of applications in biosensors,[1a] energy system,[1b] catalysis,[1c] and in self-assembly of supramolecular structures.[1d] Nanostructured platinum metals materials are very attractive because of their superior electrocatalytic performance than the blanket Pt electrode. Recently several methods have been reported[2] for the preparation on nanostructure but it is difficult and time-consuming to prepare the nanostructures. Besides, platinum is very expensive, resource limited and irreversibly inactivated by CO-like poisoning species. Therefore, it is essential that the utilization of platinum should be kept as low as possible without sacrificing the catalytic performance. The one best way to accomplish this is to create continuous Pt island networks. The interconnected structure could have additional advantages in enhancing catalytic activities for reactions that involve two or more reactants, because such networks supply enough absorption sites for reactant molecules over a close range.[3] Here, we report a new and simple method for fabricating continuous Pt island networks by pulse-potentiostatic electrodeposition using Si substrates of low resistivity, which act as the current collector. And thus, the silicon support was very appropriate for use as the Pt electrocatalytic electrode in respect of electrical conductivity. As shown in Scheme 1, the presence of the surface oxide layer on the silicon substrate can greatly enhanced the oxidation of CO adsorbed on the active Pt sites according to the bifunctional mechanism. Moreover, the electrocatalytical study of the continuous Pt island network on the silicon substrate indicates the potential application for electrodes in direct methanol fuel cells.



Scheme 1 Schematic illustration of the continuous Pt island network on the flat silicon substrate. The right hand side exhibits the bifunctional mechanism of CO electrooxidation. The adsorbed oxygen containing species on the surface of SiO_2 can facilitate the oxidation of CO-like poisoning species adsorbed on the active Pt sites.

The fabrication steps for the continuous island Pt network electrode are described in the following: a flat Si substrate was washed with acetone followed by DI water (18 MΩ), then etched in 10 wt% HF at room temperature for 5 min to remove the thin native oxide layer on the silicon surface. Then, the Pt particles were electrodeposited on the etched Si in the aqueous solution of 1 M K_2PtCl_6/1 M H_2SO_4 (100 mL/100 mL) at room temperature by potentiostatic pulse plating in a three electrode cell system with a saturated calomel reference electrode (SCE).[4] The time durations for the high potential pulse (+0.08 V) and the low potential pulse (−0.01 V) were 3 ms and 1 ms, respectively. The blanket Pt catalyst were prepared by potentiostatic pulse plating (1 M K_2PtCl_6/1 M H_2SO_4) on the silicon substrate. The time durations for the high potential pulse (+0.06 V) and the low potential pulse (–0.04 V) were 5 ms and 2 ms, respectively. The Ru decorated blanket Pt electrode was obtained by deposition of Ru on the blanket Pt by potentiostatic pulse plating at −0.07 V and +0.02 V in a 1 M $RuCl_3$ (200 mL) solution for 5 ms and 1 ms, respectively. The catalyst mass loading (mg cm^{-2}) was calculated by measuring the difference in the mass of the electrodes before and after the Pt deposition, using a micro-balance (Sartorious, PB-SAH) with a resolution of 0.001 mg. The mass loading of Pt on the continuous island Pt network/Si, the Ru decorated Pt film/Si, and the blanket Pt on silicon electrodes are ~0.37 mg cm^{-2}, ~0.89 mg cm^{-2}, and ~0.94 mg cm^{-2}, respectively.

Fig. 1(A) and (B) illustrates a representative scanning electron microscopy (SEM) image of the blanket Pt on silicon substrate and Ru decorated on blanket Pt, respectively. From the SEM images, the blanket Pt and the Ru decorated on the blanket Pt were completely covered on the silicon substrate after the electrochemical deposition. Fig. 1(C) show the surface morphology of the pulse electrodeposited Pt on the Si substarte. The Pt islands are mutually connected over the Si substarte. The Pt islands forming the continuous Pt island film have size distribution from ~200 nm to ~800 nm. X-Ray photoelectron spectroscopy (XPS) shown in Fig. 1(D) indicated that Pt and Ru were successfully deposited on the silicon substrate by the pulse electrodeposition.

The electroactive surface area (ESA) of the electrodes was determined by the CO-stripping cyclic voltammetry, which was

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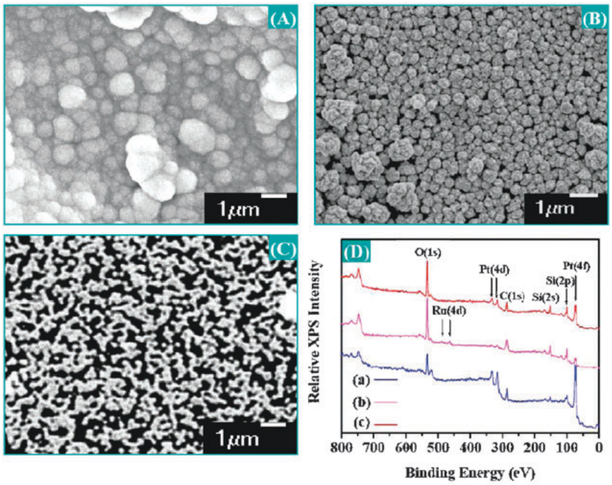

Fig. 1 SEM images: (A) blanket Pt on flat Si substrate; (B) Ru on blanket Pt; and (C) continuous Pt island network on the flat silicon substrate; (D) X-ray photoelectron spectrum (XPS) of (a) blanket Pt/Si; (b) Ru decorated blanket Pt; and (c) continuous Pt island network.

performed by flowing a 10% CO/N_2 gas mixture in the 1 M H_2SO_4 aqueous solution at +100 mV for 35 min, using a Pt wire as the counter electrode and a saturated calomel reference electrode (SCE). Before scanning, the solution was purged with N_2 gas for 30 min to removed CO remained in the solution. Representative CO-stripping voltammograms for the continuous Pt island network/Si, the Ru decorated Pt film and the blanket Pt/Si electrodes are illustrated in Fig. 2(A).

A high ESA of 67 $m^2 g^{-1}$ was obtained for the continuous Pt island network/Si electrode by integrating the CO-electrooxidation peak of first CO stripping cycle, assuming an oxidation charge value of 420 µC cm^{-2} for a monolayer of CO adsorbed on a smooth platinum surface.[5] The ESA of the continuous Pt island network/Si electrode is much higher than that of the Ru decorated Pt film electrode (21 $m^2 g^{-1}$) and that of the blanket Pt electrode (16 $m^2 g^{-1}$). This shows that the continuous Pt island network/Si electrode has a relatively high ESA, most likely due to the interconnect structure of the Pt islands. Such well-defined continuous Pt island network structure provides abundant active sites for the electrooxidation reaction of methanol.

From the CO-stripping curve, we noticed a lower onset potential and smaller peak potential for CO oxidation on the continuous Pt island network electrode in comparison to the Ru decorated Pt film and the blanket Pt film/Si. Examination of the CO oxidation curves reveals that the onset potential of the continuous Pt island network/Si electrode (∼0.43 V) is lower than that of the Ru decorated/Pt (∼0.48) and the blanket Pt/Si (∼0.60 V). The CO oxidation peak potential for the continuous Pt island network/Si (∼0.57 V) is also lower than that for the Ru decorated Pt (∼0.60 V) and the blanket Pt/Si (∼0.64 V), probably due to an enhanced CO oxidation rate on the Pt islands surrounded by the chemical SiO_2 layer, which was formed on the Si substrate in the electrolyte. The presence of the oxide layer on the silicon substrate can promote the oxidation of CO adsorbed on the active Pt sites *via* the bifunctional mechanism.[4] The oxygen-containing species on SiO_2 (such as hydroxyl surface group) can transform CO-like poisoning species adsorbed on Pt to CO_2, releasing the active sites on Pt for further electrochemical reaction, and hence the continuous Pt island network on the flat Si substrate possess higher activity towards CO oxidation compared to the blanket Pt on silicon and the Ru decorated Pt film.

Fig. 2(B) shows the cyclic voltammograms of the three electrodes recorded in 1 M CH_3OH/1 M H_2SO_4 aqueous solution at a potential scan rate of 20 mV s^{-1}. The CV curve of the continuous Pt island network/Si shows that the methanol oxidation peak had the maximum around 0.63 V *vs.* SCE and a very low onset potential of ∼0.38 V. Also shown in Fig. 2(B) is the CV curves of the blanket Pt film and the Ru decorated Pt film, which show a much smaller current density with a higher onset potential. The negative onset potential shift indicated that the continuous Pt island network/Si can effectively reduce overpotentials in the methanol electrooxidation reaction.[6]

Noted that the methanol oxidation peak in the forward scan for the continuous Pt island network/Si electrode was much larger than the peak in the region of 0.3–0.5 V in the reverse scan. In the cyclic voltammetric scan, the anodic peaks in the forward scan and in the reverse scan are associated with electrooxidation of methanol and removal of incompletely oxidized carbonaceous species (CO-like poisoning species) on the electrode, respectively. The catalyst tolerance against CO adsorption may be evaluated by the ratio of the current density of the forward anodic peak (I_f) to that of the reverse anodic peak (I_b), (I_f/I_b).[7] For the continuous Pt island/Si electrode, the (I_f/I_b) ratio was calculated to be ∼19. This ratio was more than 9 times and 20 times larger than that of the Ru decorated Pt film and the blanked Pt film, respectively.

Chroamperometry technique was employed to further test the activity of theses three electrodes. Fig. 2(C) shows the chronoamperogram of electroactivity of the three electrodes at the oxidation potential of ∼0.4 V in the 1 M CH_3OH/1 M H_2SO_4 aqueous solutions at 25 °C. Steady-state currents for methanol electrooxidation were measured for more than 800 s. At the oxidation potential of 0.4 V, the steady-state currents at 800 s for the continuous Pt island network/Si, Ru decorated Pt film and blanket Pt/Si are ∼10 mA cm^{-2}, ∼4 mA cm^{-2}, and ∼0.05 mA cm^{-2}, respectively. The observation implied that most CO-like poisoning species could be oxidized and removed from the Pt catalyst so that the catalytic oxidation of methanol could be kept proceeding efficiently on the continuous Pt island network/Si electrode. Because oxygen containing species on the SiO_2 surface layer can promote the CO removal as described above, the improvement of the electrooxidation activity can be ascribed to the synergistic effect of the Pt island catalyst and the SiO_2 surface layer. These results are very consistent with the CV studies shown in Fig. 2(A) and (B).

Tafel plot for electrochemical oxidation of 1 M CH_3OH/1 M H_2SO_4 aqueous solution at a scan rate of 1 mV s^{-1} is shown in Fig. 1S in the ESI.† The blanket Pt/Si and Ru decorated Pt film have a Tafel slope of ∼115 mV/dec and ∼137 mV/dec, respectively. On the other hand, the continuous Pt island network/Si exhibits a much larger Tafel slope (∼245 mV/dec), suggesting a great difference in the electrooxidation mechanism for the continuous Pt island network/Si electrode from the other two electrodes. This might be ascribed to the Pt island network structure and the presence of active oxygenated on the SiO_2 surface layer.[8] The mechanistic difference could result in the better catalytic activity and CO tolerance of the 2-D

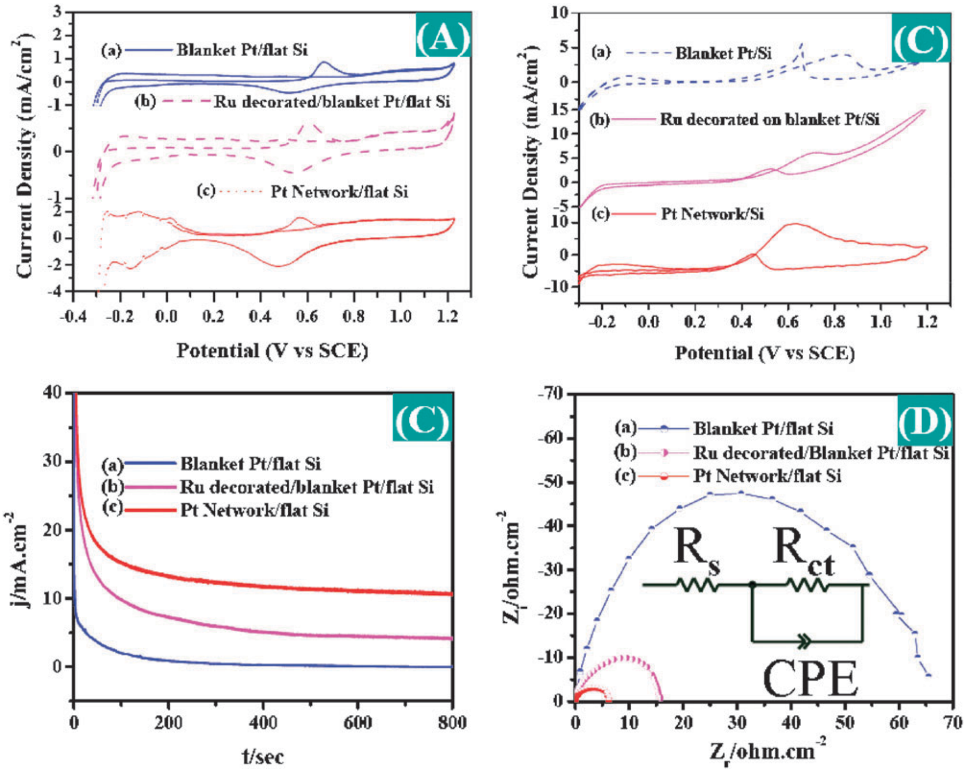

Fig. 2 Electrochemical measurements of: (A) CO stripping cyclic voltammetry curves recorded at room temperature in a CO saturated 1 M H_2SO_4 solution at a scan rate of 20 mV s^{-1}; (B) cyclic voltammograms in 1 M CH_3OH + 1 M H_2SO_4 at a scan rate of 25 mV s^{-1}; (C) chronoamperometry at the potential of 0.4 V; (D) electrochemical impedance spectra in 1 M CH_3OH + 1 M H_2SO_4 at the potential 0.3 V. The inset in Fig. (D) shows the equivalent circuit model.

continuous Pt island network/Si electrode compared to the blanket Pt/Si and the Ru decorated/Pt film electrode.

The electrochemical impedance spectroscopy (EIS) measurements were used to evaluate the charge-transfer resistance and the capacitance of these three electrodes during methanol electrooxidation.

Fig. 2(D) shows three Nyquist plots recorded in 1 M CH_3OH/1 M H_2SO_4 at the oxidation potential of ~0.3 V, where Z_r and Z_i represent the real and imaginary components of the impedance, respectively. The equivalent circuit model shown in the inset of Fig. 2(D) was used to fit the experimental data. The R_s resistor represents the resistance of the electrolyte solution, R_{ct} the charge transfer resistance and CPE represents the constant phase element.[2e] As shown in Fig. 2(D), the EIS well fits with the proposed model. The Ru decorated Pt film and the blanket Pt/Si electrodes have charge-transfer resistances about $\sim 16\ \Omega\ cm^{-2}$ and $\sim 68\ \Omega\ cm^{-2}$, which is over 3 times and 11 times larger than that for the continuous Pt island network/Si ($\sim 6\ \Omega\ cm^{-2}$).

In summary, two-dimensional continuous island Pt network electrode have been successfully fabricated by potentiostatic pulse plating on the flat silicon substrate, and electrochemical measurements confirm that this catalyst structure on the silicon substrate has a better electroactivity toward methanol oxidation than the blanket Pt/Si and the Ru decorated Pt film/Si electrodes. The good electrooxidation performance can be ascribed to the synergistic effect of the Pt island catalyst and the surrounding SiO_2 surface layer, which significantly enhanced the CO tolerance and thus improved the electrooxidation activity of the Pt catalyst.

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