

Synthesis of transferable nanoporous PtFe/Au film with enhanced electrocatalytic activity

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An ordered nanoporous PtFe/Au film is synthesised via a simple two-step strategy based on sputtering and electrochemical deposition onto anodic aluminium oxide template. The morphology image of PtFe/Au film is characterised. The results reveal that the prepared porous film consists of ordered hexagonal array of nanoholes with a pore diameter of 40 nm and a periodic distance of 120 nm. PtFe/Au film after dissolving the template can maintain its integrity and is transferable. The PtFe/Au nanoporous film based electrode shows high catalytic activity for oxidation of methanol in alkaline ambience which making it more attractive for fuel cell operations.

1. Introduction: Numerous efforts have been employed in controlling the sizes, shapes and compositions of inorganic nanomaterials in the past few decades, because these parameters represent key elements that determine their properties. Because of the auspicious electrocatalytic properties of methanol oxidation [1–3], the suitable design of Pt-based nanostructures has earned decreasing interest lately. Alloying Pt with low-cost 3d transition metal can develop the electrocatalytic action through a bifunctional mechanism [4, 5] and reduce noble metal wastage. It has been proclaimed that because of its superior half-wave potential, lessened catalyst cost and enhanced OH resistance [6], the 3d transition metal, Fe, has a serious synergistic catalytic result in the methanol oxidation reaction (MOR) proposition. Luo *et al.* [7] for instance presented a higher specific activity and stability through synthesising PtFe nanotubes/graphene hybrid than the commercial PyRu/C catalyst. On the other hand, utilising PtFe/C cathodes, Scott *et al.* presented a higher power density of up to 30% compared with that of Pt/C cathode [8]. By optimising the morphology of the catalysts [9, 10], an improvement to increase the catalytic quality of the assigned materials is still possible.

Owing to their particular properties and promising utilisation in optoelectronic devices, photonic crystals and catalysis, ordered porous films have gained considerable attention lately. Aside from that, they are considered as an excellent substrate for surface-enhanced Raman spectroscopy (SERS) [11, 12]. A compelling way to engineer the physical and chemical properties [13] is to add the nanometer sized artificial void in this film. The template-supported approach when talking about fabrication methods for the synthesis of this class of nanoporous film is a powerful approach since it is not just uncomplicated and cheap, but it also has an accurate control over the film's void size [14, 15]. In the present work, we introduce a simple two-step method based on anodic aluminium oxide (AAO) template to synthesise ordered nanoporous PtFe/Au film. The prepped porous film after dissolving the template could retain its wholeness and be moved to another substrate. The system can then be benefited as an effective electrocatalyst for oxidation of methanol if the porous PtFe/Au film is debilitated onto the ITO glass.

2. Experimental details: As explained in the reports beforehand, an anodisation process refined the AAO templates [16, 17]. So as to release the mechanical stress and appropriately electropolish to a mirror finish, the cleaned high-purity aluminium sheets (99.999%) were annealed at 450°C in vacuo for 5 h and subsequently electropolished in a 1:9 volume mixture of

perchloric acid and ethanol at 25 V for 5 min. At about 8°C, the first step of anodisation brought out for 6 h at 50 V in a 0.3 mol/l oxalic acid electrolyte. Then, the original film was put into a solution made up of chromic acid (1.8 wt%) and phosphoric acid (6 wt%) at 60°C for 9 h. Under the same conditions, the second anodisation carried out. Subsequently, after removing the remaining Al using SnCl₄ solution, the distance between two adjacent channels in the templates would be about 120 nm and the diameter of channels would be about 70 nm.

In Fig. 1, the preparation process for PtFe/Au nanoporous film is illustrated. To provide a conductive electrode and also a electrodeposition substrate, a thin layer of Au with about 30 nm in thickness was sputtered onto the head side of the template. Utilising a three-electrode system with a carbon plate as a counter electrode and Ag/AgCl electrode as the reference electrode, PtFe alloy was electrodeposited onto the Au layer. The electrodeposition was then executed in an aqueous mixture consisting of 0.5 mol/l FeSO₄•7H₂O, 0.02 mol/l FeCl₂•4H₂O, 1.54 mmol/l H₂PtCl₆•6H₂O and 0.04 g/L C₁₂H₂₅SO₄Na. The potentiostatic deposition was achieved at –1.0 V for 4 min while the PH value of the mixture was adjusted to 2.5 by 2 mol/l H₂SO₄.

As presented in Fig. 2a, a free and stable film was figured after an ordered nanoporous alloy film was detached from the template by floating on the surface of 2 mol/l NaOH aqueous solution to dissolve the AAO for few minutes. Through lifting it off on a water surface and picking it up together with an auxiliary substrate, the PtFe/Au film can be transported essentially from one substrate to another [15]. Like ITO glass, ITO/PET and a glass rod, these substrates perhaps can be flat or bent (presented in Figs. 2b–d, successively).

Once the transferred film completely dried, there would form a strong binding force (Van der Waals' force) between the film and the substrate, which can promise the feasibility of practical application of the film. Moreover, the product presented here is very soft and pliable. A bent PET/ITO substrate deposited with FePt/Au nanofilms demonstrates the as-prepared electrode with a satisfactory adaptability, as presented in Fig. 2c. As seen from Fig. 3, the nanoporous film shows how it maintains its wholeness and continuity, even though it is bent over or doubled up. A distended application may result from that character. The PtFe/Au film was deposited on flat glass with the same process for comparison. The ordered nanoporous Pt/Au film was also synthesised and then transferred onto ITO substrate.

The final products were characterised by X-ray diffraction (XRD, Shimadzu 7000). Scanning electron microscopy (SEM, JSM-7100F)

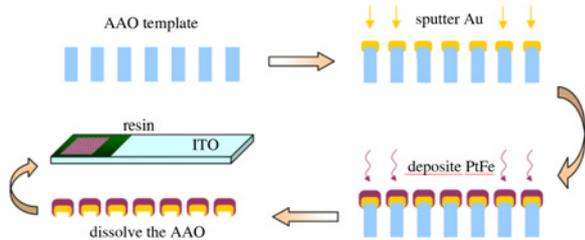


Fig. 1 Scheme of the template preparation for PtFe/Au nanoporous film

analysis equipped with an energy dispersive X-ray spectroscopy (EDS) was performed. Electrocatalytic measurements were carried out on CHI 660E electrochemical workstation based on a conventional three-electrode system with Pt wire as the counter electrode, Ag/AgCl electrode as the reference electrode and the prepared electrode as the working electrode.

3. Results and discussion: Fig. 4a shows the resulting overview SEM image of the product after the template is dissolved and the film is transferred onto an ITO glass. It can be seen that the as-prepared porous film is arranged in an ordered hexagonal close-packed pores array, maintaining the AAO template's geometrical ordering. The porous film as magnified in Fig. 4b shows mountain-shaped, with ups and downs on the surface. The adjacent pores exhibit an approximate 120 nm period distance in agreement with that of the template. Enclosed by six mounds, each pore reveals a roughly 40 nm average diameter. The porous film shows quite a rugged topography due to its grainy surface, which increase its surface area greatly. It can be observed that the vertical height of the rolling film is about 100 nm.

Fig. 5a indicates the XRD pattern of the porous film. The peaks are still identifiable even if they appear to be faint. Beside Au diffraction peaks coming from Au layer sputtered onto the template as substrate, the other diffraction peaks should be caused by the alloy film synthesised here. It is apparent that there is a change in the peaks in the direction of the higher diffraction angles of the porous film as compared with pure Pt, revealing a formation of an alloy between Fe and Pt. As can be seen, there is an absence of the Fe characteristic lines. With further observation and analysis, it is apparent that the peaks resemble tetragonal crystalline FePt alloy (JCPDS Card No. 89-2051). A complementary EDS analysis validates the hypothesis. As seen in

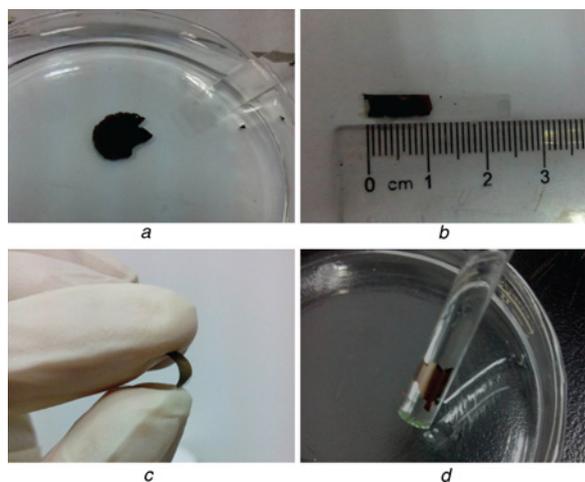


Fig. 2 Photographs showing the transfer of the nanoporous PtFe/Au film
 a Film floating on NaOH solution
 b Film immobilised on a ITO glass
 c Film immobilised on a flexible ITO/PET
 d Film immobilised on a glass rod

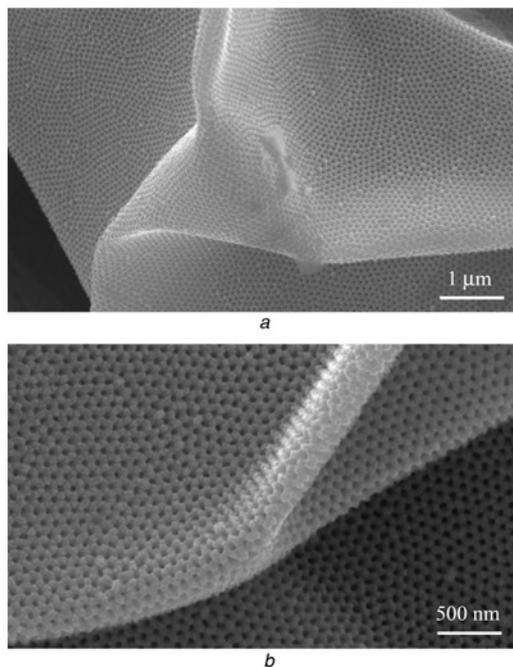


Fig. 3 SEM images showing the bent PtFe/Au film

Fig. 5b, Pt and Fe are indeed present in the typical EDS spectrum. The average atom ratio of Pt and Fe is decided to be 2:1 by quantitative analysis of the EDS system.

A useful electrocatalyst for the oxidation of methanol can be employed from the system where the porous PtFe/Au film is immobilised onto ITO glass. Through cyclic voltammetry (CV)

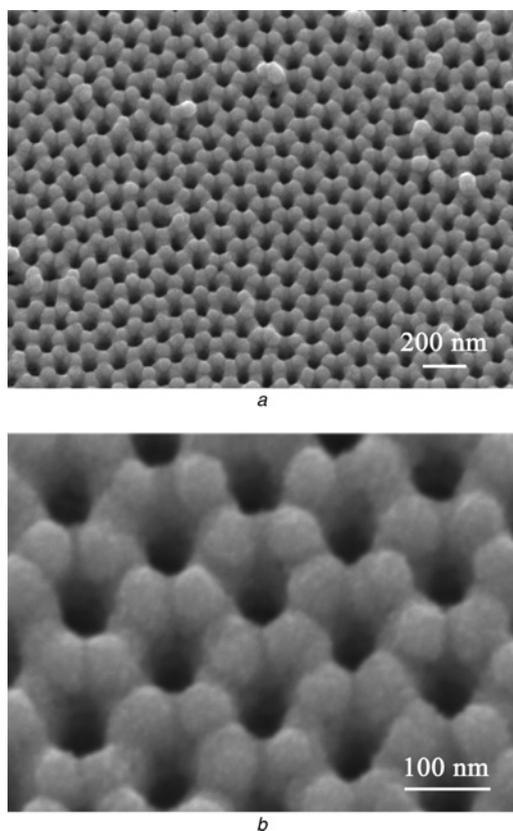


Fig. 4 Resulting overview SEM image of the product after the template is dissolved and the film is transferred onto an ITO glass and porous film as magnified shows mountain-shaped, with ups and downs on the surface
 a Low-magnification SEM image of the nanoporous PtFe/Au film
 b High-magnification SEM image

technology, the catalysis activity of our product for methanol oxidation was studied. The CV curves of ordered nanoporous PtFe/Au film in the absence and presence of 0.5 mol/l methanol in 0.5 mol/l KOH solution are shown in Fig. 6a. It can be observed in the forward scan that a high peak current density (59.0 mA/cm²) of oxidation occurs at 0.2 V. The hydrogenation of methanol [18, 19] cause this phenomenon. However, when the incompletely oxidised carbonaceous species is removed, a comparatively weaker oxidation current density (2.4 mA/cm²) occurs at -0.15 V in the reverse branch. This finding is different from earlier reports [20, 21]. There has not been a particular and detailed study to discover what precisely causes this effect. However, we put forward the conjecture that it may have been caused when the methanol dehydrogenation process is facilitated by the hydroxide groups in alkaline media and the oxidation of CO species is removed throughout the MOR [22]. The special nanoporous structure and component of PtFe/Au film presented here may be also important factors in reducing the adsorptions of CO species. The bare ITO electrode was tested and there was no methanol oxidation peaks. This further shows that for methanol oxidation, the bare ITO has no electrocatalytic activity. In Fig. 6b, it can be seen that a small current for methanol oxidation was detected when the nanoporous Au film was tested on bare ITO electrode, implying only a faint electrocatalytic activity of the nanoporous Au film for methanol oxidation. As a result, we come to the conclusion that the porous PtFe film has high catalytic activity toward methanol electrooxidation in alkaline media. It should be noted that PtFe nanoporous film electrode showed a greater negative shift of the oxidation potential than the nanoporous Au film (0.7 V), suggesting high electrocatalytic activity for methanol oxidation.

In Fig. 6c, the results are shown for the comparative study on the catalytic activities of PtFe/Au film with flat surface and Pt/Au film with ordered nanoporous structure. Both the ordered nanoporous Pt/

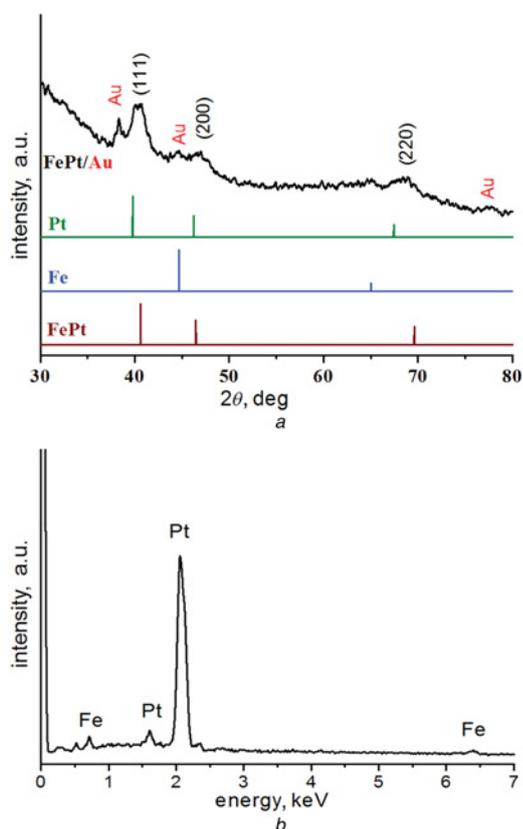


Fig. 5 XRD pattern of the porous film and Pt and Fe are indeed present in the typical EDS spectrum
a XRD pattern
b EDS spectrum of the nanoporous PtFe/Au film

Au film (10.9 mA/cm²) and the plane PtFe/Au film (2.87 mA/cm²) have smaller peak current density than that of ordered nanoporous PtFe/Au film. It is notable that the ordered nanoporous PtFe/Au film and plane PtFe/Au film have similar contents. The porous characteristic of ordered nanoporous Pt/Au film accounts for its higher electrocatalytic activity. This porous structure increases its surface area, thereby boosting its electroactivity [13]. It can also be concluded that the existence of Fe will improve the oxygen reduction reaction activity of Pt, as proven by the variation in electrocatalytic activity between ordered nanoporous Pt/Au film and ordered nanoporous PtFe/Au film. It is apparent that the presence of Fe in the Pt-based catalysts causes the diminishing of the onset potential and the enhancement of the catalytic activity via the synergistic effect, wherein the adsorption of oxygen species comes with much-

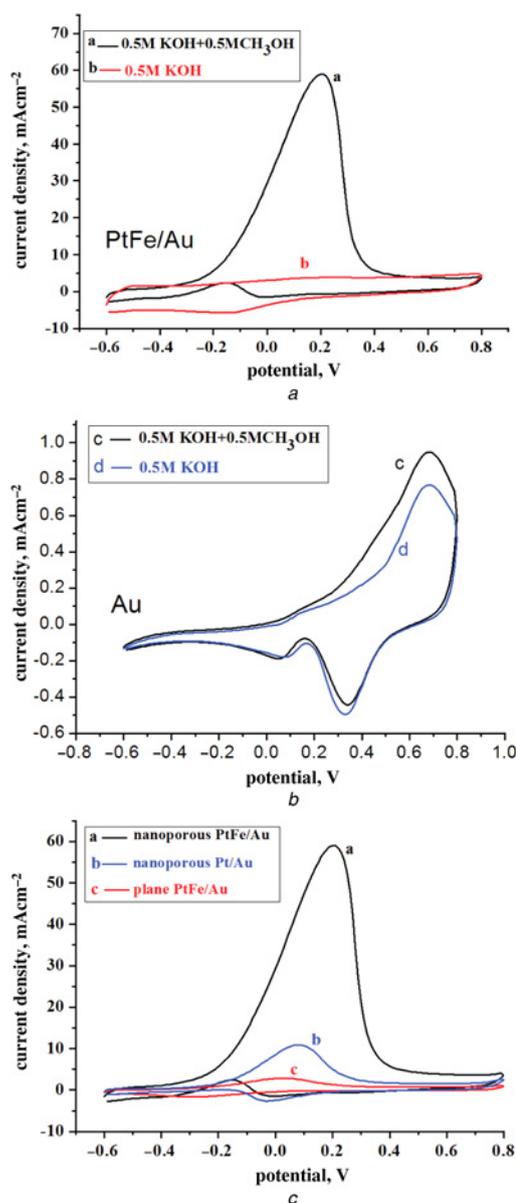


Fig. 6 The electrochemical properties were studied by CV method and the results show that the porous PtFe film has higher catalytic activity toward methanol electrooxidation in alkaline media
a CV curves of ordered nanoporous PtFe/Au film in the absence and presence of 0.5 M methanol in 0.5 M KOH solution
b CV curves of nanoporous Au film in the absence and presence of methanol
c CV curves of ordered nanoporous PtFe/Au, ordered nanoporous Pt/Au, and plane PtFe/Au catalysts in 0.5 M KOH containing 0.5 M methanol, (scan rate: 100 mV/s)

Table 1 Comparison of electrochemical catalytic performance based on Pt-based micro/nanomaterials

Electrode materials	Peak potentials, V	Peak current, mA cm ⁻²	Reference
Porous Pt nanotubes	-0.2	5.0	[27]
Nanoporous PtRuCuW alloy	0.6	1.8	[28]
nanoporous PtCu microwires	0.7	4.9	[29]
Pt nanoparticles/ITO	0.71	47.4	[23]
PtNi nanosheets/ITO	0.75	17.4	[24]
Nanoporous PtFe/Au film/ITO	0.2	59.0	this work

diminished potential on the additive Fe rather than on Pt [7, 8]. Moreover, similar to that of the nanoporous PtFe/Au film, in the reverse branch, the oxidation peak of PtFe/Au film with flat surface and Pt/Au film with ordered nanoporous structure are both very weak. Again, they indicate that the alkaline media, special morphology and component have important effect on reducing the adsorptions of CO species and strengthening poisoning-tolerance.

There have been a number of reports on the production of Pt-based nanoporous materials and Pt-based nanomaterials deposited on ITO glasses. These studies reveal favourable results for methanol oxidation [23–29]. To compare the electrochemical catalytic performances in these reports with our result, the peak potentials and peak currents in CV responses are summarised in Table 1. It can be found that the nanoporous PtFe/Au film reported in this study clearly has a low peak potential with higher peak current density, indicating the higher catalytic activity. Besides the important role of Fe existed in our product, we believe that the distinct structure of the PtFe nanoporous film is a contributing factor since the surface area can expand with the porous film structure, thereby boosting the electroactivity. As a result, the simple fabrication and the good electrocatalytic ability of ordered nanoporous PtFe/Au film help it in developing superior electrode material for alkali-type fuel cell applications.

4. Conclusion: This work shows that an AAO template-based two-step method is used to synthesise ordered nanoporous PtFe/Au film. A practical and useful electrocatalyst for oxidation of methanol in the alkaline medium can be achieved by transferring the PtFe/Au film onto an ITO substrate after dissolving the template. Exhibiting superior electrochemical activity and effective transferability, the resulting product as presented here may be able to translate into other iterations in electroanalytical chemistry applications, even leading to the creation of innovative electrochemical biosensors.

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