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All-Metal Layer-by-Layer Films: Bimetallic Alternate Layers with Accessible Mesopores for Enhanced Electrocatalysis

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Supporting Information

ABSTRACT: We have prepared multilayer mesoporous bimetallic (Pt/Pd) alternating films by layer-by-layer (LbL) electrochemical deposition. Because of the high surface area and heterometallic interfacial atomic contacts, enhanced electrocatalytic activity for methanol oxidation reaction is realized. This novel LbL approach allows optimization of the electrocatalytic performance through precise tuning of the thickness of each layer.

Although we clearly understand the importance of nanostructural controls for advanced functions,[1] easy fabrication methods for designed nanostructures are in fact rare. One satisfactory methodology is the "layer-by-layer" (LbL) approach for the fabrication of nanometer-level layered structures in a designable manner.[2] The high versatility of the LbL approach[3] has resulted in the proposal of different formation mechanisms through utilization of various interactions, including electrostatic interactions,[4] hydrogen bonding,[5] metal coordination,[6] and charge-transfer interactions,[7] as well as chemical reactions, such as the click reaction,[8] electrochemical coupling,[9] and sol—gel reactions.[10] As another feature, the fuzzy nature of the structural formation provides rather disordered interfacial structures in LbL films,[11] which is advantageous for a chemical process based on interlayer molecular diffusion but is a serious problem for the formation of neat interfacial structures, such as the atomic-level contacts necessary for enhanced interlayer electrical communication. To overcome this disadvantage in the typical LbL technology, we here propose a method for the fabrication of all-metal mesoporous LbL films in which both atomic-level interlayer metal-to-metal contacts and facile diffusion through the mesopores are assured.

Our target in this work was the preparation of bimetallic alternating layers with advanced functions, such as superior electrocatalysis. Pt-based bimetallic materials have recently attracted considerable attention because of their advanced performance in catalysts, fuel cells, gas sensors, and biosensors. In comparison with a Pt-only system, bimetallic systems with various metal compositions can provide more attractive opportunities for further enhanced performance.[12] Recent reports have demonstrated that the Pt—Pd heterointerface exhibits particularly remarkable advantages in various applications, especially an improved electrocatalytic activity in the methanol oxidation reaction.[13] Therefore, forming alternating-layer structures with nanometer-level layer thicknesses is highly advantageous for achieving an abundant heterointerface by atom-level interfacial contact. To enhance further the Pt electrocatalytic performance, increasing the accessible surface area is the most important goal. This can be accomplished by introducing mesopore structures into the metallic layers. In this research, we accomplished these demands through the preparation of Pt/Pd bimetallic alternating layers with mesopores by combining two concepts: the LbL approach and the electrochemical deposition method.

The electrochemical method for fabricating Pt/Pd bimetallic alternating layers with mesopores is illustrated in Figure 1. The mesoporous Pt and Pd layers were alternately electrodeposited from two kinds of precursors. Metallic mesoporous structures were formed with the assistance of micelle assembly in a dilute surfactant electrolyte.[14] One precursor solution was a K_2PtCl_4 aqueous solution with a Brij 58 surfactant, while the other one was a Na_2PdCl_4 aqueous solution with a P123 surfactant [for details of the procedure, see the Supporting Information (SI)].

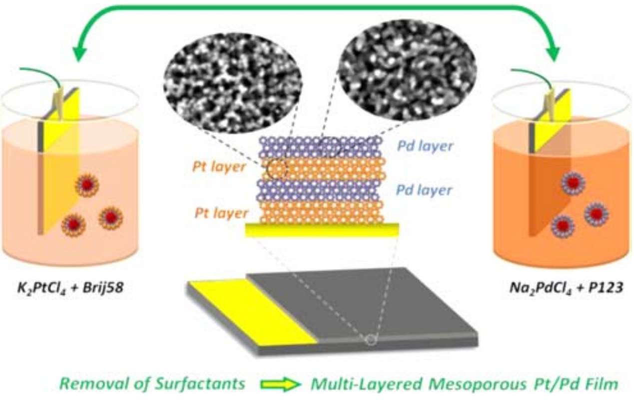

Figure 1. Procedure for fabricating multilayer mesoporous Pt/Pd films by electrochemical deposition.

First, mesoporous Pt and Pd films were separately prepared, and their surface morphologies were directly observed by

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scanning electron microscopy (SEM). Both films adhered very well to the substrates (Figure S1a,b in the SI) and had many mesopores that were uniform in size (Figure S2). The thicknesses of the mesoporous Pt and mesoporous Pd films increased linearly with the deposition time (Figure S1c). We could increase the film thicknesses until the metal sources were used up. However, when the film thicknesses were greater than 2 μm, we observed some cracks on the film surface. To evaluate the mesostructural orderings in the two films, mesoporous Pt and Pd films were measured by low-angle X-ray diffraction (XRD) (Figure S3). The obvious peaks were observed, and their *d* values were calculated to be about 7 nm for the Pt layer and 10 nm for the Pd layer, which coincided with the values observed by SEM (Figure S2). The Brunauer−Emmett−Teller (BET) surface areas for the mesoporous Pt and Pd layers were calculated to be around 45 $m^2\ g^{-1}$ and 35 $m^2\ g^{-1}$, respectively.

A series of multilayer mesoporous Pt/Pd films with different layer thicknesses were prepared by changing the deposition times (Figure 2 and Figures S4 and S5). The film thicknesses for all of the samples were around 200 nm. To observe the multilayer structures clearly, electron back-scattered diffraction (EBSD) measurements were performed on a six-layer Pt/Pd film formed by deposition for 20 s per layer (Figure 2a-2 and Figure S6). The Pt layers appear as bright regions and the Pd layers as dark regions. In total, six layers were obviously confirmed in the film. The enlarged SEM image (Figure 2b-2) shows that uniform mesopores filled the entire film, indicating that the formation of a mesoporous structure was not affected by repeated electrochemical deposition.

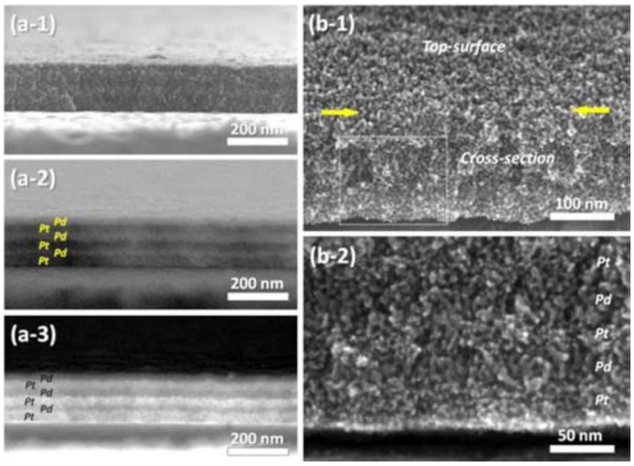

Figure 2. Images of a six-layer mesoporous Pt/Pd film: (a-1) low-magnification SEM image; (a-2) EBSD image (an enlarged image is shown in Figure S6); (a-3) dark-field transmission electron microscopy image (an enlarged image is shown in Figure S7); (b-1) high-magnification SEM image; (b-2) enlarged SEM image of the square box in (b-1).

As shown in Figure S1c, the thicknesses of the mesoporous Pt and Pd layers exhibited a linear relation to the deposition time. Therefore, by changing the deposition time, the layer thicknesses could be controlled. Even when the Pt/Pd deposition cycle was performed five times, the prepared 10-layer mesoporous film showed a flat surface without any voids and cracks, realizing a well-controlled layered structure (Figure S5). Thus, regardless of the number of Pt and Pd layers, all of the prepared films were flat on the surface, and the LbL construction could be clearly observed. Our approach not only provides a facile and efficient method for preparing well-controlled multilayer mesoporous Pt/Pd thin films but also controls the thickness of the deposited films.

Several multilayer Pt/Pd films with different layer thicknesses were further evaluated for electrocatalytic reaction (Figure 3).

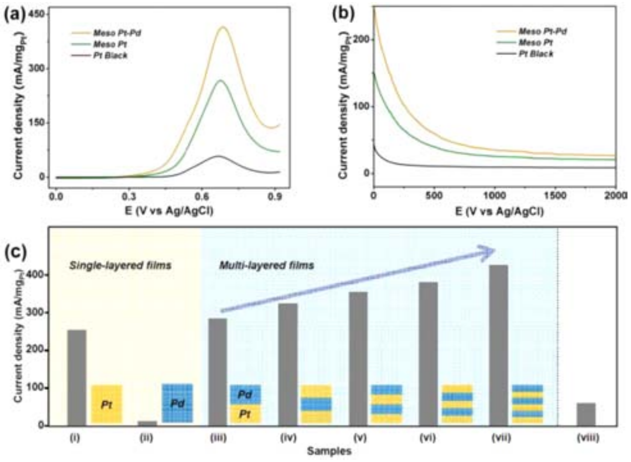

Figure 3. (a) Linear-sweep voltammograms and (b) chronoamperograms (recorded at 0.6 V) for a six-layer mesoporous Pt/Pd film, a mesoporous Pt film, and commercially available Pt black. The data were recorded in 0.5 M H_2SO_4 containing 0.5 M CH_3OH at a scan rate of 50 mV s^{-1}. The current densities (*Y* axis) were calculated by normalizing the observed currents by the mass of Pt in the films. (c) Pt mass-normalized methanol oxidation activities for (i) mesoporous Pt, (ii) mesoporous Pd, (iii) mesoporous Pt/Pd, (iv) mesoporous Pt/Pd/Pt, (v) mesoporous Pt/Pd/Pt/Pd, (vi) mesoporous Pt/Pd/Pt/Pd/Pt, and (vii) mesoporous Pt/Pd/Pt/Pd/Pt/Pd films and (viii) commercially available Pt black particles. The thicknesses of all the films were kept around 200 nm. Only the current density of mesoporous Pd film is given as "mA/mg$_{Pd}$".

As an important part in fuel cells, methanol was selected as a model molecule for studying the electrocatalytic performance. As shown in Figure 3a, in comparison with a commercial Pt black catalyst, a significant enhancement of the peak current and a negative shift of the onset potential were observed for methanol oxidation on a six-layer mesoporous Pt/Pd film (shown in Figure 2) and on a mesoporous Pt film (shown in Figure S1a). Chronoamperometric curves recorded at 0.6 V for 2000 s (Figure 3b) indicated that the current density of the six-layer mesoporous Pt/Pd film was higher than that of the mesoporous Pt film and much higher than that of commercial Pt black over the entire time range. To investigate further the catalytic performance of the multilayer films, the Pt mass-normalized current densities were calculated (Figure 3c). Notably, the mesoporous Pd film had very low catalytic activity for the methanol oxidation reaction. However, the multilayer structure showed a higher current intensity than the mesoporous Pt film. Among all the samples, the six-layer mesoporous Pt/Pd film exhibited superior catalytic activity. Thus, a multilayer mesoporous structure can effectively reduce the amount of Pt used while retaining a high level of catalytic activity.

In comparison with commercial Pt black, well-ordered mesoporous films possess much higher electrocatalytic activities for a long time, primarily because the mesostructured framework provides a large surface area and prevents undesirable agglomeration of the active sites.[14] On the other hand, the mesoporous multilayer Pt/Pd film showed higher electrocatalytic activity than mesoporous Pt (Figure 3a); this suggests that the mesoporous Pd layer plays a key role in the enhanced activity. As Figure S7 demonstrates, at the interface between the Pt and Pd layers, the atomic-level Pt-to-Pd contact was formed without any voids and holes. Therefore, the Pt and Pd atoms are miscible with each other at the interface, resulting in the formation of an inserted pseudo-Pt/Pd alloy, which is beneficial for promoting the cleavage of C−H in the methanol decomposition.[15] With an increase in the number of alternating layers, the Pt−Pd heterointerfaces also increased. Therefore, the six-layer Pt/Pd film showed higher electrocatalytic activity than any of the other Pt/Pd films with fewer layers (Figure 3c).

In summary, we have proposed a novel and facile pathway for the fabrication of Pt/Pd bimetallic alternating multilayer mesoporous films with the assistance of micelle assembly in a dilute surfactant electrolyte. Because of the synergistic effect of the high surface area and accessible Pt−Pd heterointerface, our multilayer mesoporous Pt/Pd films showed enhanced electrochemical activity in the methanol oxidation reaction. The multilayer films with thinner layers showed better catalytic activity. The thickness of each layer of mesoporous Pt and Pd can be altered by simply controlling the applied deposition time because of the linear relationship between the deposition time and the deposition thickness of the Pt and Pd layers. Our synthetic concept can be applied to more complicated multilayer mesoporous films with various metal and alloy layers. We strongly believe that such films can further improve the electrochemical activity. By optimizing the layer compositions and their thicknesses, we can realize new types of integrated sensors, sequential reactors, and electrocatalysts in the future.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures and characterization data for the obtained films. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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