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Three-dimensionally ordered mesoporous Pd networks templated by a silica super crystal and their application in formic acid electrooxidation[†]

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Three-dimensionally ordered mesoporous Pd networks fabricated by a simple reduction method in solution using a face centered cubic silica super crystal as template exhibit high electroactivity in formic acid oxidation.

Palladium plays a crucial role in organic synthesis,¹ H₂ sensing² and many industrial catalytic applications.³ It has been shown recently that Pd is also promising in direct alcohol⁴ or formic acid fuel cells (DFAFCs) applications^{5–8} which are promising power sources for portable electronics. Compared with direct methanol fuel cells, DFAFCs can be operated at a higher voltage and run more efficiently, due to the unique characteristics of formic acid such as lower crossover through the Nafion membrane and the higher kinetic activity than methanol.^{6,8} For formic acid oxidation in DFAFCs, Pd was found to exhibit superior electroactivity to the Pt catalyst.⁵ Since the activity of metals strongly depends on their morphology,⁹ considerable efforts were made to prepare metal Pd with well-defined nanostructures.

Recently, three-dimensionally ordered mesoporous (3DOM) precious metals (voids 2–50 nm) with interconnected networks have shown great potential for a wide range of applications owing to their fascinating properties inherent to the nature of the original metal along with high surface areas and ordered mesostructures.^{10,11} Although the macroporous metals (voids > 50 nm) have been widely practised,¹² the fabrication of ordered mesoporous metals is still challenging due to the narrower window size. So far, Pt and Au have been mainly reported, but the fabrication of catalytically active 3DOM Pd networks for fine chemical synthesis and fuel cells catalysis at milder conditions has not yet been reported.

Herein, we report the synthesis of 3DOM Pd networks by a simple, rapid and convenient solution reduction method using

hydrazine hydrate (N_2H_4 · H_2O) as a reducing agent and the face centered cubic (fcc) silica super crystal as a template. The interconnectivity of the Pd replica was ensured by the tight control of the concentration and volume of Pd precursor solution for impregnation to fully utilise the interstices in the silica super crystal and by selecting proper reducing agents to control the reduction of Pd and growth of Pd networks.

The preparation of the 3DOM Pd networks is as follows: silica nanoparticles with a uniform diameter of ca. 40 nm were prepared according to the literature¹³ with slight modifications. The details are described in the ESI.† The silica nanoparticles were self-assembled into a super crystal by centrifugation. A H₂PdCl₄ solution (0.56 M) was prepared at 363 K by dissolving 1.00 g of PdCl₂ in 10 ml of hydrochloric acid (37 wt%) under vigorous stirring. PdCl₂ and hydrochloric acid were both purchased from Sinopharm Group Chemical Reagent Co. Ltd. The dried silica super crystal (0.16 g, $S_{\text{BET}} =$ 77 m² g⁻¹, $V_{\text{pore}} = 0.39 \text{ cm}^3 \text{ g}^{-1}$) was then impregnated with the above H₂PdCl₄ solution (0.56 M, 0.11 mmol) with vigorous stirring by hands for 15 min and dried at 393 K for 12 h. N₂H₄·H₂O (25 wt%, 20 ml) was further added to reduce Pd²⁺ and the siliceous template was dissolved by hydrofluoric acid (20 wt%, 20 ml). The product was centrifuged, washed with distilled water for 6 times, and methanol for 3 times, and finally kept in methanol for characterization and activity test. Electrochemical measurements were performed using a standard three-electrode electrochemical cell on a CHI660B electrochemical working station in a 0.5 M $H_2SO_4 + 0.5$ M HCOOH solution (details are described in the ESI[†]).

The high-resolution scanning electron microscopy (HRSEM) images (Fig. 1a) and transmission electron microscopy (TEM) images (Fig. 2a and b) show that a highly ordered fcc silica super crystal was built from the uniform silica nanoparticles through centrifugation. After H₂PdCl₄ impregnation and N2H4·H2O reduction, HRSEM images of the Pd infiltrated sample (Fig. 1a) demonstrate that the ordered fcc lattice is well retained during the preparation. An enlarged HRSEM image (inset in Fig. 1a) shows that Pd species fill into the interparticle voids of the silica super crystal template. TEM images (Fig. 2c and d; Fig. S1, ESI⁺) further reveal that the Pd is well filled into the interstices of the silica super crystal template and highly interconnected. After the removal of the siliceous template, HRSEM (Fig. 1b and c) and TEM images (Fig. 2e and f) of the silica-free Pd sample

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[†] Electronic supplementary information (ESI) available: The details of silica nanoparticle preparation, the details of Pd electrode preparation and electrochemical measurements, the TEM images of a Pd infiltrated silica super crystal, HRTEM and EDX of silica-free 3DOM Pd networks, and TEM images of the Pt infiltrated silica super crystal. See DOI: 10.1039/clcc11652e



Fig. 1 HRSEM images of (a) Pd infiltrated silica super crystal and (b) silica-free 3DOM Pd networks. Insets in (a) and (c) are the enlarged images.

demonstrate that ordered mesoporous Pd networks were well formed. The pore wall thickness of the 3DOM Pd networks is *ca.* 3–8 nm and the mesopore diameter is *ca.* 40 nm (inset in Fig. 2f). The high resolution transmission electron microscopy (HRTEM) image (Fig. S2, ESI†) reveals that the apparent continuous Pd networks were actually formed by the aggregation of Pd nanocrystallites. Energy dispersive X-ray emission analysis (EDX) found that no silica was left in the Pd networks, verifying the complete removal of the silica template (Fig. S3, ESI†). The selected area electron diffraction (SAED) pattern (inset in Fig. 2e) of the 3DOM Pd shows a ring-like pattern with many intense spots, revealing the polycrystalline nature of the Pd networks.

To ensure high interconnectivity of Pd species to form the Pd networks, controlling the two most important experimental



Fig. 2 TEM images of (a, b) the silica super crystal template with corresponding FT patterns and projection charts (insets), (c, d) Pd infiltrated silica super crystal and (e, f) silica-free 3DOM Pd networks with an SAED pattern (inset in e) and enlarged image (inset in f). (a, c, e) were recorded along zone axis $\langle 211 \rangle$, (b, d, f) along zone axis $\langle 100 \rangle$.

parameters, *i.e.* the procedure of impregnation and type of reductant, is found to be crucially important. It was found that continuous 3DOM Pd networks could be easily obtained when using the near saturated H₂PdCl₄ precursor solution and the volume ratio of the H2PdCl4 precursor to the pore of the silica super crystal template was *ca*. three. Among N_2H_4 · H_2O , SnCl₂ and H₂, N₂H₄·H₂O was found to be the best reducing agent to form the continuous Pd networks. Our results reveal that a relatively fast reduction rate was favorable for metal Pd to form 3DOM networks with high interconnectivity, which is quite different from the case of Pt. When N₂H₄·H₂O was applied for the formation of 3DOM Pt, only Pt nanoparticles without interconnectivity were formed (Fig. S4, ESI†). The difference may be due to the slow nucleation¹² and slow crystal growth of Pt.^{11,14} Compared with the solid reduction method using dimethylamineborane (DMAB)¹¹ and the H₂ reduction method,¹² the present solution reduction method using N₂H₄·H₂O is more convenient, simple, and non-time-consuming, which is promising for the further nanostructural control of metal Pd by the templating technique.

Fig. 3a compares the formic acid oxidation activities on the 3DOM Pd networks and ultrafine Pd black electrode catalysts. The forward peak current for formic acid oxidation on 3DOM



Fig. 3 Cyclic voltammograms at a scan rate of 50 mV s⁻¹ (a) and chronoamperometric curves at 0.23 V (b) *vs*. the saturated calomel electrode measured on a glass carbon electrode modified with 3DOM Pd networks or ultrafine Pd black in a 0.5 M HCOOH + 0.5 M H₂SO₄ solution.

Pd networks is 257.4 mA mg^{-1} , which is 350% higher than that of ultrafine Pd black (56.5 mA mg^{-1}) and the corresponding peak potential of 3DOM Pd networks is located at ca. 0.23 V, ~ 30 mV more negative than that for the ultrafine Pd black catalyst. The improved electroactivity of 3DOM Pd networks may relate to the effective electronic conduction through the regular and highly interconnected networks⁸ and the electronic states of the surface atoms because of the unique morphology of the 3DOM Pd networks.⁴ The electrochemical stability of the 3DOM Pd networks and ultrafine Pd black on formic acid oxidation was also investigated by chronoamperometry (Fig. 3b). A decrease in the current density with time is found in both materials, which can be attributed to the intermediate poisoning species formed from formic acid oxidation.⁸ Nevertheless, the current decay on the 3DOM Pd networks is significantly slower than that on the ultrafine Pd black. At the end of the 1000 s test, the oxidation current on the Pd networks is ca. 23% of the initial value and considerably higher than that on the ultrafine Pd black. This shows that the ordered mesoporous structure of 3DOM Pd networks

enhances the electrochemical stability of Pd electrocatalysts for the formic acid electrooxidation reaction.

In conclusion, 3DOM Pd networks were successfully prepared by a simple and convenient solution reduction method using the interstices in a self-assembled silica super crystal and their application study for formic acid electrooxidation was initially explored. The 3DOM Pd networks appear to exhibit much better electroactivity than the ultrafine Pd black, which could be promising as an anodic catalyst for DFAFCs.

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