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Mesoporous Pt Hollow Cubes with Controlled Shell Thicknesses and Investigation of Their Electrocatalytic Performance

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Mesoporous Pt hollow cubes (MPHCs) are successfully synthesized by using surfactant micelles as the soft-template directing uniformly-sized mesopores. Silver (Ag) cubes are utilized as the hard-templates for the creation of hollow interiors.

Advances in nanotechnology have enabled the preparation of various structured nanomaterials with controllable sizes, shapes, and compositions for many applications, especially for the energy conversion usages.[1-5] Among various electrocatalysts for direct methanol fuel cells (DMFCs), which are promising energy conversion devices due to their advantages of high energy conversion efficiency, low operation temperatures, and low pollutant emissions, platinum (Pt) has been proved to be competent and efficient both for the anodic and cathodic reactions.[6-11] Despite significant progress, breakthroughs are still required to further improve the Pt utilization efficiency due to its scarcity and large demand in practical usage. For Pt electrocatalyst design toward methanol oxidation reaction (MOR), structure-controlled catalysts often show impressive enhancement in their activity and stability. A strong shape-dependent catalytic property is observed for ultrafine Pt cubic nanoboxes, even compared to the hollow spheres[12].

In recent years, mesoporous materials, especially mesoporous metals, have exhibited superior electrochemical properties due to their extremely high areas per unit volumes and unique atomic structures exposed on the pore surface.[13-16] On the other hand, hollow particles with internal cavities and controlled shell thicknesses are also effective to improve the utility efficiency of the materials.[17-19] So far, hollow particles have been generally prepared by various hard-templating methods. Hollow Au structures are prepared by using decahedra-shaped Ag templates.[20] It has been well known that Ag crystals are formed in various morphologies, such as cube, octahedral, wire, truncated polyhedral, so the use of Ag crystals as templates have showed their merits in shaping various hollow interiors.

Our goal in this study is the creation of mesoporous shells of hollow particles, which can make the entire surfaces readily accessible by the reagents, expecting unique properties caused by the combination of two different structures; hollow and mesoporous structures. Since the first report of mesoporous metals, lyotropic liquid crystals consisting of highly concentrated surfactants have been widely utilized as one of typical soft templates. However, this methodology provides very limited metal shapes, such as only irregularly-shaped particles and continuous films, which is not easily extended to more complicated architectures. Our recent developed 'surfactant micelle assembly' using low concentrated surfactants is highly useful for realizing various constructions, such as zero-dimensional (0D) nanoparticles, 1D nanorods and nanofibers, and 2D films.[21-24] Here mesoporous Pt hollow cubes (MPHCs) are prepared by using dual templating system; surfactant micelles as *soft*-template for the mesoporous shells and sacrificial Ag cubes as *hard*-template for the hollow interiors. The obtained MPHCs are expected to exhibit the highest Pt utilization efficiency in methanol oxidation reaction.

In this experimental, MPHCs were synthesized in two-step approach. Firstly, uniform Ag cubes as the hard-template for hollow interiors were synthesized by modifying a polyol process.[25] In a typical synthesis, NaHS, poly(vinyl pyrrolidone), and $AgNO_3$ were dissolved in ethylene glycol solution, respectively, and then they were successively added to pre-heated ethylene glycol solution. After that, the reaction mixture was continued with heating at 155 °C. After being cooled to room temperature, the organic molecules were completely removed by consecutive washing/centrifugation cycles. The shape and size of the synthesized Ag cubes were characterized by scanning electron microscope (SEM, **Fig. S1a**), and transmission electron microscopy (TEM, **Fig. S1b-c**). The obtained SEM images at low magnification clearly showed well-defined cubic structures with a very high yield (> 99%). The

particle-size distribution was very narrow and their average edge length was 55 nm. High-resolution TEM (HR-TEM) image and the selected-area electron diffraction (ED) patterns exhibit the single crystallinity of the obtained Ag cubes. The wide-angle X-ray diffraction (XRD) spectrum (**Fig. 1a**) confirmed the face-centered cubic (*fcc*) structure of Ag without any difference compared to the standard one.
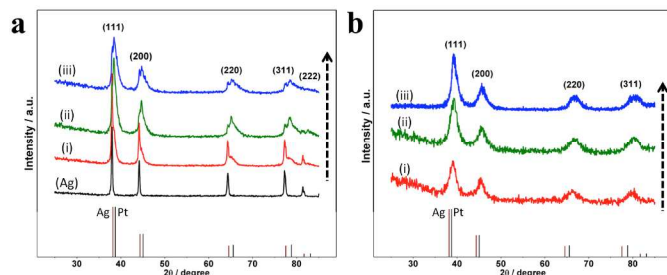

Fig. 1 | Wide-angle XRD patterns of (a) as-prepared Ag@Pt cubes with different shell thicknesses ((i) 5.0 nm, (ii) 5.5 nm, and (iii) 6.0 nm, respectively) and (b) the corresponding MPHCs after removing the Ag cores. The samples are prepared by using different amounts of Pt precursor ((i) 0.8 µmol, (ii) 1.2 µmol, and (iii) 1.6 µmol K_2PtCl_4, respectively.). XRD peaks theoretically observed for Ag and Pt *fcc* crystals are noted, and the XRD pattern for Ag cores themselves is also shown in panel (a).

The growth of mesoporous Pt layer on the Ag cubes was carried out by using nonionic surfactant (Brij 58) as the soft-template. In a typical synthesis, the Ag cubes were dispersed in deionized water with a 1 mg·mL^{-1} concentration. Then, Brij58, deionized water, K_2PtCl_4, and ascorbic acid were successively added to the Ag cube suspension. After 5 hours, the mesoporous Pt layer completed to grow on the Ag cube surface. Then, the obtained Ag@Pt cubes were mixed with an excess amount of concentrated nitric acid solution, and the mixture solution was stirred for 3 days at room temperature, allowing selective dissolution of the Ag core. Ag can be dissolved in nitric acid or NH_4OH. After the removal of the Ag cubes, MPHCs were obtained, as shown in **Fig. 2**. Every particles possess cubic hollow interiors which are identical or similar to the Ag sacrificial templates. A strong contrast between the edge and the centre indicates the formation of a hollow structure in the interior. It is noted that our MPHCs show definitely cubic cavities, which are quite different from previously reported Au boxes prepared through galvanic replacement reaction on Ag cubes.[26-27] Since a redox potential of $[AuCl_4^-/Au]$ (0.99V *vs.* SCE) is significantly higher than that of $[Ag^+/Ag]$ (0.80 V *vs.* SCE), galvanic replacement reaction between $AuCl_4^-$ species and Ag cubes can easily take place. In our case, however, the redox potential of $[PtCl_4^{2-}/Pt]$ (0.76 V *vs.* SCE) is lower than that of $[Ag^+/Ag]$ (0.80 V *vs.* SCE). Therefore, galvanic replacement reaction cannot take place in the present work.

The thickness of mesoporous Pt shell can be controlled by changing the used amount of K_2PtCl_4 precursor. The shell thicknesses were varied from 5.0 nm (with 0.8 µmol K_2PtCl_4) to 5.5 nm (with 1.2 µmol K_2PtCl_4) and 6.5 nm (with 1.6 µmol K_2PtCl_4), respectively (**Fig. 2**). When the amount of Pt precursor was increased to 6.0 µmol, a very thick shell was formed (**Fig. S2**). Further increase in the amount of Pt precursor (over 8 µmol)

led to the presence of mesoporous Pt nanoparticles detached from the Ag cubes as a byproduct.
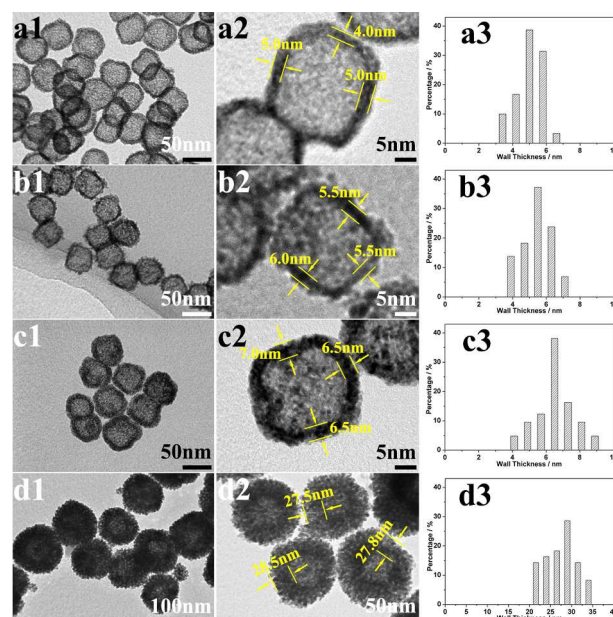

Fig. 2 | TEM images with different magnifications of the obtained MPHCs with various shell thicknesses, and the corresponding shell thickness distribution. The samples are prepared by using different amounts of Pt precursor ((a) 0.8 µmol, (b) 1.2 µmol, (c) 1.6 µmol, and (d) 6.0 µmol K_2PtCl_4, respectively). Their average shell thicknesses are varied from (a) 5.0 nm, (b) 5.5 nm, (c) 6.0 nm, and (d) 28 nm, respectively.
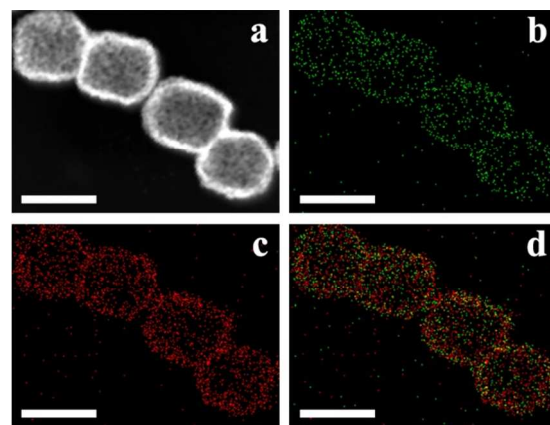

Fig. 3 | (a) High-angle annular dark-field scanning TEM (HAADF-STEM) image of the obtained Ag@Pt cubes prepared by using 0.8 µmol K_2PtCl_4. (b-c) Nanoscale elemental mapping of (b) Pt and (c) Ag, and (d) overlapping image of Pt and Ag elements. Scale bar is 50 nm.

Ag@Pt core-shell cubes (before removal of Ag cores) with the smallest shell thickness were characterized by elemental mapping. Both Pt and Ag content were distributed uniformly throughout the entire cubes (**Fig. 3**). Although the Pt signal shows enhancement only at the edge parts, the boundary between Pt and Ag domains is not obviously observed, meaning the formation of very thin Pt layers. **Fig. 1a** shows wide-angle XRD

patterns for Ag@Pt cubes (before removal of Ag cores) with various Pt thicknesses. With the increase of Pt shell thicknesses, the Pt and Ag peaks are more clearly separated. This is the direct evidence of the formation of Ag@Pt core-shell architecture (*not* Ag-Pt alloy form). After treatment under concentrated HNO_3 solution, only the Pt phase remained, and no Ag phase was observed (**Fig. 1b**). The elemental mapping after HNO_3 treatment clearly supported the complete removal of Ag cores (**Fig. S3**).

Our MPHCs with mesoporous shell are quite different from cubes and tubes previously reported.[28-29] The abundance of mesopores on the surface of each cube is a crucial factor to enhance the catalytic performance, since the mesopores can increase the specific surface area and allow for rapid transportation of reagents. To confirm the formation of mesoporous architecture, low-angle X-ray diffraction (XRD) measurement was carried out (**Fig. S4**). Broad peaks were confirmed in the 2θ range from 1.0 to 1.5°. The *d*-spacing of the peaks is found to be around ~7.5 nm which corresponds to the pore-to-pore distance. Considering the pore wall thickness (around 1~2 nm), the average pore size is estimated to be approximately 6 nm, which coincide with the ideal pore size prepared by using the same Brij 58 micelles through constant potential deposition.[21-24] Brij 58, a typical nonionic surfactants, is the key factor to form mesoporous structures. When no Brij 58 surfactants were used under the same experimental condition, hollow Pt cubes without any mesoporous structure were obtained (**Fig. S5**).
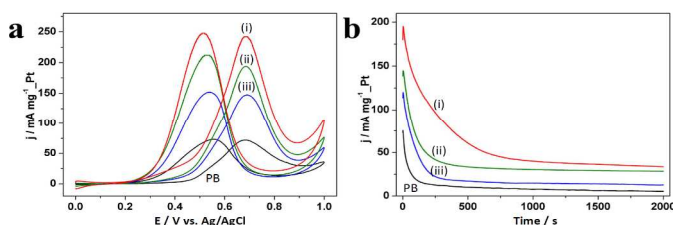

Fig. 4 | (a) Cyclic voltammograms, and (b) chronoamperometric curves (recorded at 0.6 V) for methanol oxidation reactions catalyzed by MPHCs with different Pt shell thicknesses ((i) 5.0 nm, (ii) 5.5 nm, and (iii) 6.0 nm) and Pt black (PB, black line), respectively, in 0.5 M H_2SO_4 solution containing 0.5 M methanol. The current densities (Y-axis) are normalized by the mass of Pt (mg).

The electrocatalytic performance of our MPHCs was evaluated. The electrochemical surface area (ECSA) of the obtained MPHCs was studied. After the careful calculation, the MPHCs showed very high ECSA for each sample ((i) 50.2 $m^2 \cdot g^{-1}$_Pt, (ii) 48.6 $m^2 \cdot g^{-1}$_Pt, and (iii) 47.3 $m^2 \cdot g^{-1}$_Pt) (**Fig. S6**). Both of their activity and stability towards the methanol oxidation reaction (MOR) were further tested and benchmarked against commercially available Pt black (PB). The cyclic voltammograms (CVs) shown in **Fig. 4a** exhibit the typical features of MOR on Pt catalysts, which possesses two obvious anodic peaks in the positive and negative sweeps. With the increase of the shell thicknesses, the mass-normalized current densities were gradually decreased from 242.0 $mA \cdot mg^{-1}$_Pt to 193.8 $mA \cdot mg^{-1}$_Pt and 147.3 $mA \cdot mg^{-1}$_Pt in the positive direction sweep. The results clearly demonstrate that our MPHCs with the smallest shell thickness (around 5 nm) are much more active and durable electrocatalysts for MOR. This activity greatly exceeds commercially available PB catalyst (72.0

$mA \cdot mg^{-1}$_Pt). It was further noted that the catalytic performance of our MPHCs is much higher than that of the state-of-the-art Pt-based electrocatalysts, such as hollow Pt nanospheres/carbon nanotubes hybrids[30], Au-Pt yolk-shell structures[31], mesoporous Pt nanoparticles[21], and mesoporous Pt films[23] (all the measurements described in the literature were done in 0.5 M methanol). The observed enhancement of MPHCs on MOR is likely to be caused by the combination of mesoporous structure and hollow interior.[32] Such hierarchical porous architectures can indeed improve the diffusion/transport of reagents and make a significantly large active surface accessible by the reagents. In addition, the fairly thin Pt walls are interconnected, which is beneficial for a superior stability by avoiding aggregation. Therefore, our MPHCs showed much higher activity and stability toward MOR (**Fig. 4b**).

As can be seen in **Fig. S7**, MPHCs were highly crystallized. Overall, the lattice fringes coherently extended across the mesopores. A large amount of distortions, atomic defects, and strain/stress were observed, which would be caused by the large lattice difference between Pt and Ag crystals. In general, kink and step sites are more active in the catalysis. In the case of MOR, they surely help in breaking C-H bonds during methanol decomposition, thereby improving the activity toward MOR.[33-35]

In conclusion, MPHCs were successfully fabricated by using the micelles as pore directing soft-template and the Ag cubes as hard-template. Our synthetic method allow to control the mesoporous Pt shell thicknesses from 5 nm to 29 nm. The obtained MPHCs with the smallest shell exhibited the highest activity and durability in MOR. Through this study, the superior electrochemical performance is ascribed to a synergetic combination of mesoporous structures and hollow inner cavities. Tailored design of Pt electrocatalysts in the present work will play an important role in the future applications with higher Pt utilization efficiency.
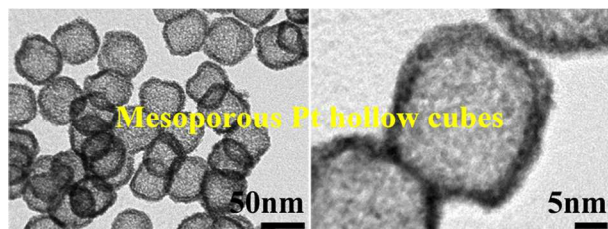
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