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Open-Mouthed Metallic Microcapsules: Exploring Performance Improvements at Agglomeration-Free Interiors

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Abstract: Although artificial capsule structures have been thoroughly investigated, functionality at the surfaces of their interiors has been surprisingly overlooked. In order to exploit this aspect of capsular structure, we here report the breakthrough fabrication of metallic (platinum) microcapsules with sufficient accessibility and electroactivity at both interior and exterior surfaces (open-mouthed platinum microcapsules), and also we demonstrate improvements in electrochemical and catalytic functions to emphasize the practical importance of our concept. The open-mouthed platinum microcapsules were prepared by template synthesis using polystyrene spheres, where surface-fused crystalline nanoparticles formed a capsule shell. Subsequent removal of the polystyrene spheres induced formation of mouth-like openings. The open-mouthed platinum microcapsules exhibit a substantial increase of their electrode capability for methanol oxidation and catalytic activities for carbon monoxide (CO) oxidation. Notably, activity loss during CO oxidation due to undesirable particle agglomeration can be drastically suppressed using the open-mouthed microcapsules.

As exemplified by living cells, capsular structures lead to sophisticated functions which depend on differentiation between the interior and exterior environments as well as specific interactions occurring at the capsule shell interface. Organic mimics of cells including lipid vesicles[1] and polymer capsules[2] have been widely investigated, and hollow spheres composed of hybrids and inorganic materials including silica,[3] carbon,[4] quantum dots,[5] and metal[6] have been also developed in order to compensate for the relative mechanical weakness of the organic counterparts. Some of these exhibit excellent properties suitable for drug delivery, sensing, and reactor applications.[7] Interestingly, most of these functions rely only on permeation control through the capsule membrane and/or specific interactions at their outer surfaces. Functionalities of inner surfaces of artificial capsular structures have not been fully explored except for some pioneering examples[8] although biological cells effectively use inner surface functions as can be seen in signal transduction and photoenergy conversion. Considered simply, effective use of capsular inner surfaces could double the available functionality relative to traditional systems, which rely only on use of exterior surfaces. Additionally, the interior surface environment is not susceptible to particle agglomeration.

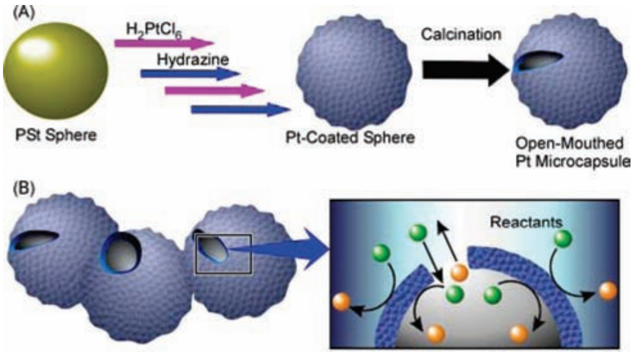

Figure 1. (A) Synthetic scheme for open-mouthed Pt microcapsules and (B) their usage for inside/outside active reactor.

In order to develop this unexplored breakthrough concept, we here report fabrication of metallic (platinum) microcapsules with sufficient accessibility to their interiors and with a variety of functions at both interior and exterior surfaces, which we refer to as open-mouthed platinum microcapsules, and we also demonstrate improvements in the electrochemical and catalytic functions emphasizing the practical importance of our concept. So far, different platinum nanomaterials[9] including nanosheets and nanoparticles have been used in several applications including fuel cells and catalysts in automobile technologies because of their high surface areas, which are however often subject to deterioration caused by their agglomeration. On the contrary, interior surfaces of hollow structures would be *completely free from* the surface area loss associated with particle agglomeration. In a clear demonstration of the advantages of our concept, the open-mouthed platinum microcapsules fabricated in this research showed a significant increase (substantially more than a 2-fold improvement) in their electrochemical and catalytic capabilities. In the latter, the open-mouthed platinum microcapsules exhibited a particularly enhanced activity in carbon monoxide (CO) oxidation at a rather low reaction temperature, thus providing a potential ideal solution for the relevant automobile technologies.

As illustrated in Figure 1, the platinum-coated polystyrene (PSt) latex spheres were first prepared by suspension of the template PSt spheres in an ethanolic solution of H_2PtCl_6 (PSt/H_2PtCl_6 = 1:3 w/w) at room temperature, followed by drying at 60 °C for 12 h with subsequent reduction using hydrazine solution.[10] The black platinum-coated PSt spheres obtained were calcined by heating to 500 °C with a heating rate of 5 °C min^{-1} and then maintained at 500 °C for 6 h, resulting in platinum microcapsules as a black powder,

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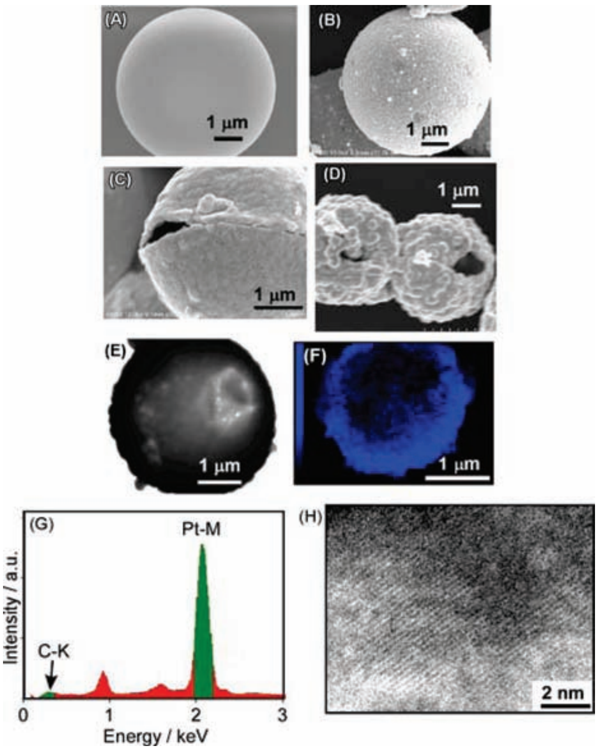

Figure 2. Morphologies: (A) FE-SEM image of PSt template; (B) FE-SEM image of Pt-coated sphere; (C and D) open-mouthed Pt microcapsule, (E) TEM image of the open-mouthed Pt microcapsule; (F) Pt distribution in EDS elemental mapping of the open-mouthed Pt microcapsule; (G) EDS spectrum of the open-mouthed Pt microcapsule; (H) high resolution TEM of {200} plane of the open-mouthed Pt microcapsule.

which were finally washed with distilled water and absolute ethanol prior to further characterization.

Field emission scanning electron microscopy (FE-SEM) images revealed that spherical morphologies with several μm diameters were maintained before (Figure 2A) and after Pt coating (Figure 2B). While the surfaces of the original PSt spheres are very smooth, coating with Pt leads to an increase in surface roughness, due to the presence of many nanoparticles with diameters ranging from 20 to 60 nm. Calcination to remove the PSt template induced interesting changes in their morphologies; i.e., the spherical shape was maintained but mouth-like openings could be observed in each sphere (see Figure 2C and 2D). Pt particles do not fully melt under the calcination conditions applied but may be surface-fused through low-temperature welding as has been reported for other metallic nanoparticles.[11] Fusion between Pt particles leads to shells free of small pores in contrast to organic capsules and mesoporous capsules, and this probably results in formation of the mouth-like openings caused by escaping residues of the decomposing template. In fact, most of the capsule objects have one or two mouth-like structures. The thickness of the open mouth sphere is 40 to 50 nm by SEM observation. The thickness can be controlled by the ratio between PSt and H_2PtCl_6 and the number of the coating cycles. The FT-IR spectrum[10] of an uncalcined sample shows clear peaks assignable to PSt templates at 696, 756, 1068, and 3025 cm^{-1} due to the phenyl group and peaks at 2848 and 2920 cm^{-1} due to the C−H vibrations. All of these peaks disappeared after calcination, indicating complete removal of the PSt template.

Further investigation by transmission electron microscopy (TEM) confirms the hierarchic structure of the hollow capsules composed of Pt nanoparticles (Figure 2E). Elemental mapping (Figure 2F) by energy dispersive X-ray spectroscopy (EDS) indicates homogeneous distributions of platinum in the open-mouthed microcapsules, although only a small amount of carbon could be detected (see EDS spectrum, Figure 2G). High resolution TEM (HRTEM) imaging (Figure 2H) revealed a regular {200} lattice plane with a *d*-spacing of 0.196 nm. In a powder X-ray diffraction (XRD) pattern,[10] all peaks could be perfectly indexed to the fcc structure of crystalline Pt.[12] The high definition of the XRD peaks attests to the high purity and crystallinity of Pt in the capsule.

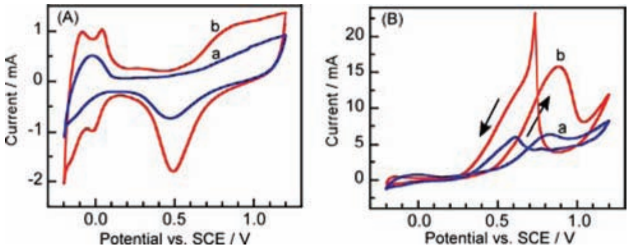

Figure 3. Cyclic voltammograms in (A) aqueous H_2SO_4 solution (0.5 M) and (B) H_2SO_4 (0.5 M) solution containing methanol (1 M) at scan rate of 25 mV s^{-1} at room temperature, as measured using a glassy carbon electrode coated with a (a) Pt-coated sphere and an (b) open-mouthed Pt microcapsule.

Cyclic voltammetric curves of electrodes coated with either uncalcined spheres or the open-mouthed capsules in 0.5 M aqueous H_2SO_4 solution showed two broad peaks in the potential range from −0.20 to 1.10 V (Figure 3A). These cathodic and anodic current densities at the same Pt content in both the hydrogen adsorption/desorption and oxide formation/reduction regions of the open-mouthed capsules are much larger than those of uncalcined spheres (ca. 2.5-fold increase). This clearly indicates a larger electroactive surface area[13] and easy accessibility to the Pt capsular surfaces due to the open-mouthed morphology. Their performance was further investigated by applying them in an electrochemical reaction in an aqueous solution of 0.5 M H_2SO_4 containing 1 M methanol (Figure 3B). Both the Pt hollow capsules and uncalcined Pt spheres exhibited catalytic activity for the electro-oxidation of methanol. Again, a much higher current density for methanol electro-oxidation was observed for the open-mouthed capsules relative to the uncalcined Pt spheres. The enhanced electroactivity of open-mouthed capsules clearly confirms the advantages of using the interior surfaces of the open-mouthed capsule structures in electrochemical applications.

The catalytic performance of the open-mouthed Pt microcapsules in the gas phase was investigated in the oxidation of carbon monoxide (CO) by oxygen (O_2). Time courses of CO conversion (Figure 4), which are normalized for the net amount of Pt, indicate that Pt on the polymer sphere showed twice the CO oxidation rate at any duration time compared to a standard catalyst (pure Pt powder, average particle diameter: 6 μm) owing to the greater surface roughness and/or the smaller particle size in the former case. Surprisingly, the open-mouthed Pt capsules exhibited significantly superior catalytic activities to both the Pt on the polymer spheres and Pt powder. Enhancement of the catalytic activity in the open-mouthed Pt capsules relative to the Pt-coated spheres reaches ca. 5-fold, which is much greater than the difference between their apparent surface areas (<2). In addition, the open-mouthed Pt capsules showed significant CO oxidation catalytic activity at an onset temperature (temperature at which 1% CO was converted) of 125 °C, which is much lower than the values reported previously for bulk Pt or Pt-supported catalysts (>200 °C).[14] It is known that one of the biggest challenges for exhaust catalysts is minimization of thermal agglomeration of the catalytic centers at elevated temperatures, which results in significant degradation of

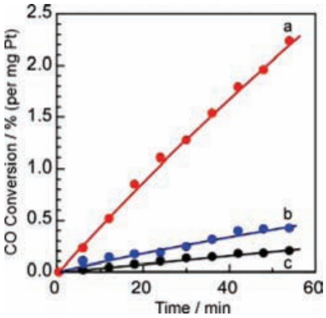

Figure 4. Time course conversion of CO oxidation at 125 °C normalized by Pt content: (a) open-mouth Pt microcapsule; (b) Pt-coated sphere; (c) Pt powder.

the apparent activity.[15] The interior surface of the open-mouthed capsules is most likely free from thermal agglomeration since it is isolated from the other capsules by the exterior surface. The very high CO oxidation activity of the open-mouthed capsules can be ascribed to the highly active, agglomeration-free interior surface. The open-mouthed Pt capsules have great potential as an exhaust catalyst, in terms of the high CO removal activity and the superior tolerance to thermal agglomeration of the active sites. We should emphasize again the following fact. The activity ratio of the open-mouthed capsule to Pt-coated sphere remains ca. 2.5-fold in application at room temperature (Figure 3), but it reached up to ca. 5-fold for functions at elevated temperature (Figure 4). It means that the open-mouthed structure is much more advantageous in applications at higher temperature where thermal agglomeration of particles becomes a serious problem.

This research reports a strategy for formation of open-mouthed metallic microcapsules where the advantages of using the interior surface of microcapsules in electrochemical and gaseous catalytic applications are clearly demonstrated. Because of its simplicity and ease of implementation, the concept of effective use of capsule interior surfaces can be extended to general applications including sensors, functional electrodes, and reactors. In addition, use of both interior and exterior surfaces of thin capsule shells could also lead to more effective use of scarce natural resources, in this case the precious element platinum. As demonstrated here, the huge increase of CO oxidation activity by the open-mouthed Pt capsules suggests especially that this concept may provide ideal solutions to demands in practical applications such as exhaust catalysts for automobile technologies. As known in actual uses, the apparent activity of the practical catalysts is strongly enhanced by alloying Pt nanoparticles with Pd and/or Rh. Our synthetic strategy for capsular catalysts would be widely applicable to the alloys of Pt, Pd, and/or Rh to realize much superior activity in future than that of the pure Pt material at present.

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Supporting Information Available: Synthetic details and additional characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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