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Hollow Nanostructures Very Important Paper

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## **Delicate Control on the Shell Structure of Hollow Spheres Enables Tunable Mass Transport in Water Splitting**

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Abstract: In the study of structure-property relationships for rational materials design, hollow multishell structures (HoMSs) have attracted tremendous attention owing to the optimal balance between mass transfer and surface exposure. Considering the shell structure can significantly affect the properties of HoMSs, in this paper, we provide a novel one-step strategy to continually regulate the shell structures of HoMSs. Through a simple phosphorization process, we can effectively modify the shell from solid to bubble-like and even duplicate the shells with a narrow spacing. Benefitting from the structure merits, the fabricated CoP HoMSs with close duplicated shells can promote gas release owing to the unbalanced Laplace pressure, while accelerating liquid transfer for enhanced capillary force. It can provide effective channels for water and gas and thus exhibits a superior electrocatalytic performance in the hydrogen and oxygen evolution reaction.

**R**egulating material structure according to the targeted applications has demonstrated to be an effective strategy for achieving superior performance. Besides tuning the structure of building blocks, the rational design on the architecture of the assemblies can also deliver great contribution for performance enhancement.<sup>[1,2]</sup> HoMSs, the micro-nano architecture with interior cavities as well as multiple shells spatially ordered from outside to inside, have been proved to be able to realize the optimization in mass transfer and effective surface area exposure, beneficial for many applications.<sup>[3–5]</sup> As a key parameter of HoMSs, the micro-nano structure of shell is significantly important for mass transport, but rarely studied

due to the lack of efficient strategies for precise structure control. In this work, we provide a facile one-step approach to continuedly regulate the shell structure of HoMS. In detail, we introduced the phosphorization reaction into Co<sub>3</sub>O<sub>4</sub> HoMSs, and discovered the geometrical shells structure of HoMSs evolved from solid to bubble-like, subsequently these "bubbles" fused together forming close duplicated shells, and it returned to a solid one in the end (Scheme 1). This structure evolution is experimentally realized for the first time, and then these materials were conducted for a typical multi-phase reaction of water splitting.<sup>[6]</sup> Benefitting from the structure advantages, the CoP HoMSs with close duplicated shells facilitate the escape of gas bubbles because of unbalanced Laplace pressure,<sup>[7]</sup> and enhance the driving force for liquid diffusion<sup>[8]</sup> due to capillary action, thus achieving excellent catalytic performance in both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER).

Co<sub>3</sub>O<sub>4</sub>-HoMSs were prepared by sequential templating approach (STA)<sup>[9]</sup> (Figure 1a, Figure S1). In the subsequent phosphorization process,<sup>[10]</sup> because the Co atoms in  $Co_3O_4$ spread out rapidly while P atoms diffused slowly inward,<sup>[11]</sup> a cavity was formed inside the nanoparticles and these hollow ones crosslinked together forming bubble-like structure in the shell (B-CoP-HoMSs) (Figure 1b). With the phosphorization period prolonged, these bubbles fused together and developed into CoP HoMSs with close duplicated shells (D-CoP-HoMSs) (Figure 1c), doubling the former number of shells. Moreover, D-CoS<sub>2</sub>-HoMSs can be also prepared with the similar approach by replacing the NaH<sub>2</sub>PO<sub>2</sub>·H<sub>2</sub>O with sulfur powder (Figure S2,S3). The high-magnification TEM image of D-CoP-HoMSs shows the interspacing of  $\approx 30$  nm (inset in Figure 1c). Further phosphorization promoted the fusion of close duplicated shells into a solid layer (CoP-HoMSs) (Figure 1d), resulting the same number of shells as half of D-CoP-HoMSs. The transition process can also be revealed by the respective grinding samples and HoMS at different phosphorization stages (Figure S4-S8). Additionally, benefiting from the controllability of STA, hollow sphere and double-shelled Co<sub>3</sub>O<sub>4</sub>-HoMSs, and the corresponding B-CoP-HoMSs, D-CoP-HoMSs and CoP-HoMSs (Figure S9-S12) were also successfully fabricated.

From the spherical-aberration-corrected high-angle annular dark-field scanning TEM (HAADF-C<sub>s</sub>-TEM) of B-CoP-HoMSs (Figure 1e), the bubble-like structure can be more clearly observed. The typical boundary between CoP and CoO (Figure 1 f) observed from  $C_s$ -TEM reflects the intermediate stage during the composition conversion process. These heterogeneous compositions are further converted to pure CoP after the further phosphorization (Figure S13). The

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**Scheme 1.** Illustration of the formation process of CoP HoMSs with different micro-nano structure of shells. The shells transformed from solid to bubble-like, and then the walls of these bubbles fused together forming close duplicated shells, and to the solid one at the end. The narrow cavity between the shells of D-CoP-HoMSs can accelerate liquid transfer through enhanced capillary force according to the equation of the liquid height induced by capillary force,  $h = 2\sigma \cos\theta/(\rho gr)$ , where the height (*h*) is inversely proportional to the capillary radius (*r*). Bubbles are generated by catalysis on the surfaces of HoMSs. Because of the strong confinement effect, the confined space between shells of D-CoP-HoMSs will resist the overgrowth of bubbles within shells while the bubbles outside would grow to the larger ones. According to Young-Laplace equation,  $P_s = 2\gamma/R$ ,  $P = P_0 + P_s$ , there is a pressure difference between the small bubbles on the inner surface and the connected large bubbles on the outer surface, leading to the diffusion of gas molecules from the small bubbles to the larger ones, and then the large bubbles on the outside will be quickly released due to the aerophobic surface, which can accelerate the gas releasing.



**Figure 1.** a–d) Low- and high-magnification (inset) TEM images of  $Co_3O_4$ -HoMSs and samples after phosphorization reaction for 2 h (B-CoP-HoMSs), 4 h (D-CoP-HoMSs), and 8 h (CoP-HoMSs) under 300 °C in Ar atmosphere. The scale bar of inset images is 50 nm. e–h) HAADF-C<sub>s</sub>-TEM images of B-CoP-HoMSs and D-CoP-HoMSs. i) XRD patterns, j) FT-EXAFS at the Co K edge and k) XPS curves of different samples.

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lattice spacing of D-CoP-HoMSs is  $\approx 0.166$  nm (Figure 1 g,h), corresponding to the distance between (020) planes of orthorhombic CoP. As further proved by XRD (Figure 1i, Figure S14), both CoO and CoP can be observed after phosphorization reaction for 2 hours. Further phosphorization can thoroughly complete the composition conversion from CoO to CoP and no additional peaks of impurities can be observed from the XRD patterns of D-CoP-HoMSs and CoP-HoMSs. The particle sizes of various samples also reflect the evolution of the micro-nano structure of HoMSs. Based on the Scherrer equation, the sizes of nanoparticles are calculated to be 9.8 nm, 11.4 nm, 16.1 nm for B-CoP-HoMSs, D-CoP-HoMSs and CoP-HoMSs, respectively, indicting the longer phosphorization period can induce nanoparticles to attach with each other and fuse to larger ones. The extended X-ray absorption fine structure (EXAFS) spectroscopy was further performed to investigate coordination environment of the Co species. As shown in Figure 1j, the Fourier-transformed (FT) curve of  $Co_3O_4$  appears a peak at 1.4 Å, corresponding to the Co-O coordination. As the phosphorization proceeded, the dominated peak at 1.7 Å in B-CoP-HoMSs, D-CoP-HoMSs and CoP-HoMSs can be corresponded to the Co-P coordination.<sup>[12]</sup> In the Co K-edge Xray absorption near-edge structure (XANES) spectrum (Figure S15), the absorption edge of the prepared CoP HoMSs is located in the left of CoO, implying the valence state of Co atom is between Co<sup>0</sup> and Co<sup>2+</sup>.<sup>[13]</sup> Similarly, the peaks at 779.6 and 781.1 eV in high-resolution X-ray photoelectron spectroscopy (XPS) spectrum of Co 2p (Figure 1k) can be assigned to  $Co^{3+}$  and  $Co^{2+}$  in  $Co_3O_4$ -HoMSs, respectively. With the phosphorization proceeding, the peak at 779.6 eV gradually shifted to a lower energy, which can be attributed to the decreasing of valence value of Co elements.<sup>[14]</sup> In addition, the newly appeared peak at 793.2 eV can be attributed to the formation of Co-P bond. With the prolonged phosphorization period, the ratio of the peak area of Co-P to Co-O increased (Table S1), which is consistent with the XRD, elemental mapping images and corresponding line profile analysis (Figure S16), indicating the composition transition process.<sup>[15]</sup> The oxidized species in CoP samples originate from the surface oxidization caused by the air contact.<sup>[16]</sup> Moreover, the binding energy of Co-P shows a positive deviation from the Co metal, while the P 2p has a negative shift from the base P (Figure S17). These results indicate that electrons transferred from Co to P, making Co electron deficient and P electron rich, thus facilitating the charge transfer in electrocatalysis.<sup>[17]</sup>

As a typical multi-phase catalytic reaction, electrochemical water splitting including HER and OER was investigated on different HoMSs with different shell structures.<sup>[18]</sup> The D-CoP-HoMSs show the highest catalytic activity with smallest overpotentials of 93 and 294 mV at the current density of 10 mA cm<sup>-2</sup> for HER and OER, respectively, and followed by B-CoP-HoMSs (Figure 2a and d, Table S2). The D-CoP-HoMSs present the smallest Tafel slope of 50 and 67 mV dec<sup>-1</sup> for HER and OER respectively among various HoMS samples (Figure 2b and e, Table S3), indicating the favorable electrocatalytic kinetics of this structure.<sup>[19]</sup> Notably, the results reflect after grinding, the duplicated HoMS sample has a greater drop of current density (69–83%) than those of CoP-HoMSs with solid shells (17–63%) within the selected voltage range (Figure 2 c and f). Additionally, the LSV curves and Tafel plots demonstrate that electrocatalytic properties enhance with the increase of shell number (Figure S18). Meanwhile, the D-CoP-HoMSs exhibit excellent catalytic and structural stability in both HER and OER (Figure S19–S20). Encouraged by the excellent electrocatalytic performance, we further used triple-shelled D-CoP-HoMSs as both anode and cathode to assemble a two-electrode electrolyzer for overall water splitting (Figure 2g,h). As shown in Figure 2i, the current density of  $10 \text{ mA cm}^{-2}$  can be achieved at a cell voltage as low as 1.57 V, and it shows good performance in the large current density region with excellent stability (Figure S21).

This excellent catalytic performance of the duplicated HoMSs can be understood from both the charge and mass transport. On the one hand, the electrochemical impedance spectroscopy (EIS) shows the D-CoP-HoMSs possess the lowest electron-transfer resistance (Figure 3a, Figure S22).<sup>[20]</sup> On the other hand, benefitting from the advantages of the structure, B/D-CoP-HoMSs possess higher hydrophilicity and aerophobicity compared with the CoP-HoMSs. Especially, the CoP HoMSs with close duplicated shells are better to be wetted than CoP HoMSs with porous bubble-like shells and that with non-duplicated solid shells (Figure 3b-d). The greater hydrophilicity can be understood from the equation of the liquid height induced by capillary force,  $h = 2\sigma \cos\theta/$  $(\rho gr)$ , which means the height (h) is inversely proportional to the capillary radius (r).<sup>[8]</sup> Therefore, the small space between shells of D-CoP-HoMSs can provide a stronger capillary force to drive liquid diffusion. Particularly after the release of produced gas, the liquid can rapidly replenish the space where the bubble disappears to ensure the fast reaction kinetics.

Moreover, the larger gas contact angle of D-CoP-HoMSs is in favor of the desorption of the produced gas (Figure 3eg). The similar phenomenon of gas releasing can also be observed from the in situ electrocatalytic reaction. We took the high-speed digital camara to record the bubble releasing within the electrode during potentiostatic scan and galvanostatic scan (Supporting Movies). Taking HER tested at -0.48 V vs. RHE as an example, hydrogen bubbles escaped easily from the surface of D-CoP-HoMSs with a size of  $\approx$  43 µm, close to the size of B-CoP-HoMSs ( $\approx$  47 µm), while the bubbles on CoP-HoMSs grew to larger size of  $\approx 165 \,\mu m$ (Figure 3k-m). The same tendency was observed for the oxygen bubble releasing under both the potentiostatic scan (38 µm, 39 µm, 140 µm for D-CoP-HoMSs, B-CoP-HoMSs and CoP-HoMSs at 1.92 V vs. RHE, respectively) (Figure 3km) and the galvanostatic scan (Figure S23). This phenomenon is closely related to the nucleation, growth and escape of gases. The size of bubbles can be seriously affected by the distance of the space in which they are located. Meanwhile, according to Young-Laplace equation,  $P_s = 2\gamma/R$ ,  $P = P_0 + P_s$ , where  $P_s$  is the additional pressure and R is radius of curvature, the pressure of a bubble is inversely proportional to its radius. For D-CoP-HoMSs, the confined space between shells will resist the overgrowth of bubbles within shells. The larger bubbles with lower pressure can only be generated on

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**Figure 2.** a) HER LSV and b) Tafel plots of HoMS samples before and after grinding, and Pt/C with a scan rate of  $5 \text{ mVs}^{-1}$  in 1 M KOH electrolyte. c) The current density at -0.10 V, -0.15 V, -0.20 V vs. RHE catalyzed by different samples before and after grinding during the HER. d) OER LSV and e) Tafel plots of HoMS samples before and after grinding, and RuO<sub>2</sub> with a scan rate of  $5 \text{ mVs}^{-1}$  in 1 M KOH electrolyte. f) The current density at 1.53 V, 1.58 V, 1.63 V vs. RHE catalyzed by various samples before and after grinding during the OER. g) Schematic illustration and h) optical photograph of two-electrode cell using D-CoP-HoMSs as both anode and cathode for overall water splitting. i) Polarization curves of D-CoP-HoMSs and Pt/C/RuO<sub>2</sub> for overall water splitting with  $5 \text{ mVs}^{-1}$  in 1 M KOH electrolyte.

the outer surface of HoMSs. Due to the pressure difference between the inner small and outer large bubbles, the gas molecules in the small bubbles diffuse into the large bubbles, and the large bubbles on the outside will be quickly released owing to the aerophobic surface (Scheme 1). Contrastively, because the confinement effect of CoP-HoMSs is not as strong as that of D-CoP-HoMSs, the bubbles produced on their inner and outer surface possess similar process and grow to larger size, which brings stronger adhesion,<sup>[21]</sup> thus making them more difficult to remove. Because the ion transfer coefficient *k* is positive correlation to the rate of gas escape, the rapid discharge of gas for D-CoP-HoMSs is conducive to accelerating catalytic reaction.<sup>[22]</sup>

In summary, by surveying the importance of micro-nano structure of the shell of HoMSs, we developed a novel onestep strategy to regulate the structure of shell. We systemically investigated the transition process during the phosphorization, and found the solid subunits of HoMSs, i.e.,  $Co_3O_4$ nanoparticles, transformed to hollow ones and crosslinked together, forming bubble-like structure composed of CoO and CoP, and then converted to CoP duplicated shells with a close interspace, finally the duplicated shells fused into one solid layer. We found the HoMSs with bubble-like and close duplicated shells can induce a faster reaction kinetics than the non-duplicated ones, owing to the better gas-liquid and electron transport. When applied as a bifunctional multiphase catalyst for water splitting, it manifests superior electrocatalytic activity. The geometry control in HoMS demonstrates the importance of rational design on the structure of micro-nano materials and provides an easy way for structure adjustment.

## Communications



Figure 3. a) EIS Nyquist plots of HoMS samples before and after grinding in 1 M KOH electrolyte. bd) Water contact angle images of 2 µL liquid drop on B-CoP-HoMSs, D-CoP-HoMSs and CoP-HoMSs. e-g) Bubble contact angle images of HoMSs under water. h-j) Digital photos demonstrating the hydrogen bubbles on the surface of different HoMS samples during HER at -0.48 V vs. RHE. k-m) The statistics on size distribution during potentiostatic scan at -0.48 V vs. RHE (above) for HER and 1.92 V vs. RHE for OER (bottom).

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## **Conflict of interest**

The authors declare no conflict of interest.

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