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Complex Cobalt Sulfide Nanobubble Cages with Enhanced Electrochemical Properties

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Abstract

Metal-organic frameworks (MOFs) have been widely employed as precursors to prepare various nanostructured functional materials. Here we report a “nanoparticles-in-MOF” dual-template approach for generating complex cobalt sulphide (CoS) nanobubble cages. A novel nanoparticles-in-MOF hybrid structure consisting of a Co-based MOF polyhedron host and many encapsulated mesostructured TiO₂ nanospheres is first prepared, followed by a sulfidation process to obtain a complex cage structure consisting of CoS nanobubbles in the shell. Importantly, this strategy can be extended to prepare many other functional nanoparticles-in-MOF hybrid structures. When evaluated as an electrode material for hybrid supercapacitors, the as-derived CoS nanobubble cages manifest remarkable electrochemical performance with long cycle life and good rate capability.

Keywords: MOF composites; ZIF-67; CoS; nanobubbles; hybrid supercapacitors.

The ever-growing energy demands have stimulated intense research into the development of various types of sustainable energy conversion and storage systems. In this important field, electrochemical energy conversion and storage devices^[1] that constitute an essential element in the development of sustainable energy technologies are becoming more appealing than ever. Among the electrochemical devices, hybrid supercapacitors (HSCs)^[2-4] with properties in between of batteries^[5, 6] and electrical double-layer capacitors^[7] have drawn great attention in recent years, because they can realize battery-level energy density together with high power density and long cycle life inherited from electrical double-layer capacitors. In recent years, great efforts have been devoted to develop novel electrode materials to further improve the performance of supercapacitors. Among the potential electrode materials, transition-metal sulfides (TMSs) have attracted great research interest because of their rich redox chemistry, enhanced electrical conductivity, and high capacity.^[8-10] Despite the composition control of electrode materials, the realization of high-efficiency energy storage devices also relies on delicate design of appropriate electrode architecture. Hollow structures with high surface/volume ratios, large surface areas, good permeability and abundant surface active sites have great potential in electrochemical applications.^[11-13] In particular, complex multi-shelled hollow structures have been intensively studied because this unique architecture can further improve the energy density of the electrode materials by increasing the weight fraction of the electrochemically active materials in the hollow structures.^[14-16] Despite the great progress that has been achieved, controllable synthesis of hollow particles with highly complex shell architectures towards high electrochemical performance still remains as a great challenge.

Metal-organic frameworks (MOFs) constructed from a wide range of metal species and organic ligands have recently been used as precursors for preparation of diverse hollow functional materials.^[17-28] However, conventional MOFs-derived syntheses are mainly based on a limited number of simple MOF crystals, and most of their derived hollow particles exhibit relatively simple

configurations such as single-shelled structure of one composition.^[29-32] Hybrid structures can be produced by introducing one or more different co-templates into a MOF crystal. Such elegantly designed hybrid structures with novel structures and controlled compositions are quite favorable and templates and/or precursors for the synthesis of complex hollow functional materials.

In this work, we develop a “nanoparticles-in-MOF” dual-template strategy for preparation of complex CoS nanobubble cages as an efficient electrode material for HSCs. In contrast to previous works, the present strategy first involves encapsulation of mesostructured TiO₂/hexadecylamine (TiO₂/HDA) nanospheres as the co-template in each Co-based ZIF-67 polyhedron, and transforms this hybrid precursor into hierarchical cages with CoS nanobubble subunits in the shell through a sulfidation reaction (**Figure 1**). The introduction of degradable TiO₂/HDA nanospheres into each ZIF-67 crystal provides new interfaces between the MOF host and co-templates, which favors the formation of CoS nanospecies on the interfaces to produce bubble-like subunits during the sulfidation process. Besides, this strategy can be further extended to encapsulate many other functional particles, such as Zr-based MOF nanocrystals, FeOOH nanorods, and carbon nanotubes (CNTs) into ZIF-67 crystal. Benefiting from the unique shell architecture and robust matrix, the as-prepared CoS nanobubble cages exhibit remarkable electrochemical performance when evaluated as an electrode material for HSCs.

TiO₂/HDA nanospheres are prepared through a cooperative assembly-directed process^[33] at room temperature and their surfaces are further functionalized with polyvinylpyrrolidone (PVP, Figure S1, see Supporting Information (SI)). The wide-angle X-ray diffraction (XRD) pattern (Figure S2, see SI) confirms the amorphous nature of the obtained TiO₂/HDA nanospheres. The encapsulation process is carried out by addition of Co(NO₃)₂ and 2-methylimidazole (2-MIM). In a typical synthesis, TiO₂/HDA nanospheres are mixed with Co(NO₃)₂ and 2-MIM in methanol and then kept at room temperature for 12 h without stirring. The purple product of TiO₂/HDA@ZIF-67 particles is obtained. Field-emission scanning electron microscopy (FESEM) images show the

morphology of the resultant $\text{TiO}_2/\text{HDA}@ZIF-67$ particles (**Figure 2a,b**). Compared with the ZIF-67 crystals with rhombic dodecahedral shape (Figure S3, see SI), uniform shaped ZIF-67 particles are covered with some partially embedded TiO_2/HDA nanospheres on surface. Transmission electron microscopy (TEM) images reveal that each ZIF-67 crystal contains many fully embedded TiO_2/HDA nanospheres that are distributed inside the crystal (Figure 2c,d). As revealed by powder XRD analysis (Figure S4, see SI), the $\text{TiO}_2/\text{HDA}@ZIF-67$ particles exhibit an almost identical XRD pattern as ZIF-67. The existence of TiO_2/HDA nanospheres in the hybrid structure can be further confirmed by energy dispersive X-ray spectroscopy (EDX) measurement (Figure S5, see SI). The size of $\text{TiO}_2/\text{HDA}@ZIF-67$ particles can be controlled by tuning the concentration of $\text{Co}(\text{NO}_3)_2$ and 2-MIM in the reaction system (Figure S6, see SI). Importantly, we further show that many other functional particles, including UIO-66 nanocrystals, FeOOH nanorods, and carbon nanotubes (CNTs), can also be encapsulated into the ZIF-67 crystal to form multifunctional hybrid materials (Figure S7, see SI).

The as-prepared $\text{TiO}_2/\text{HDA}@ZIF-67$ particles can withstand the solvothermal sulfidation treatment in an ethanol solution of thioacetamide (TAA). **Figure 3a** shows the FESEM image of the as-derived CoS particles at low magnification. The sample retains its morphology after the sulfidation reaction while the surfaces of the formed particles become rough (Figure 3b). From a broken cage shown in Figure 3c, the hollow interior and the nanometer-sized spherical building units can be clearly observed. The structure of the as-derived CoS nanobubble cages is further elucidated by TEM as shown in Figure 3d. The cage-shaped host and nanobubble subunits are generated as a result of the preferable formation of CoS nanospecies on external surface of MOF crystal and the interfaces between TiO_2/HDA nanospheres and MOF host respectively. A closer examination on a CoS nanobubble cage reveals the highly dispersed CoS nanobubbles throughout the cage shell (Figure 3e). The nanobubbles are composed of numerous small CoS nanoparticles (Figure 3f). The amorphous nature of the CoS materials is confirmed by powder XRD analysis (Figure S8, see SI).

EDX measurement shows that the CoS nanobubble cages contain Co and S elements with an approximately 1 : 1.3 ratio (Figure S9, see SI). The absence of peaks from Ti element suggests the complete removal of TiO₂/HDA co-templates during the sulfidation process, which is further confirmed by complete degradation of TiO₂/HDA nanospheres to TiO₂ oligomers under identical solvothermal treatment (Figure S10, see SI). The formation process of CoS nanobubble cages is proposed as follows. Specifically, the H₂S gas generated from the decomposition of TAA reacts with the outflowing Co²⁺ ions from ZIF-67 particles to form a layer of CoS on ZIF-67 particles and TiO₂/HDA co-templates. Meanwhile, the acidic H₂S causes protonation of alkylamine HDA and break coordination interaction between TiO₂ and HDA, which leads to complete degradation of TiO₂/HDA nanospheres (Supporting Discussion S1, see SI). As the reaction continues, the ZIF-67 cores and TiO₂/HDA co-templates are completely consumed, leading to the formation of CoS nanobubble cages. Different from these CoS nanobubble cages with unique morphology and complex structure, direct sulfidation of ZIF-67 crystals leads to formation of simple CoS cages (Figure S11, see SI). Therefore, the introduction of TiO₂/HDA nanospheres as the co-template is essential to ensure the formation of complex CoS nanobubble cages. As further determined by N₂ sorption measurement, the as-derived CoS nanobubble cages show much higher Brunauer-Emmett-Teller (BET) surface area of 87 m² g⁻¹ compared to 42 m² g⁻¹ for simple CoS cages (Figure S12, see SI).

The battery-type capacitive properties of CoS nanobubble cages are evaluated by using a three-electrode cell with a Pt foil as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode in 6.0 M KOH solution. A representative cyclic voltammetry (CV) curve at a sweep rate of 2.0 mV s⁻¹ in a potential window of 0 to 0.55 V is shown in **Figure 4a**, together with the CV curve of CoS cages under the same test conditions for comparison. The distinct redox peaks are attributed to the reversible Faradaic redox processes of Co²⁺/Co³⁺/Co⁴⁺ redox couples.^[3, 9] With the increasing sweep rate from 1 to 20 mV s⁻¹, the shape of the CV curves shows little evolution

except for the slight shift of peak positions (Figure S13a, see SI). Of note, the CV curves of CoS nanobubble cages enclose much larger areas than those of simple CoS cages at all sweep rates (Figure S13a and Figure S14a, see SI). Therefore, a larger amount of charges can be stored in the CoS nanobubble cages. The galvanostatic charge-discharge curves of CoS nanobubble cages in the voltage range of 0 to 0.55 V at different current densities are presented in Figure S13b (see SI). The durations for charging and discharging are almost identical at all current densities, indicating the excellent reversibility of these redox reactions. The specific capacitance as a function of current density calculated from galvanostatic charge-discharge curves (Figure S13b and Figure S14b, see SI) is plotted in Figure 4b. Specifically, the CoS nanobubble cages exhibit a high capacitance of 1060 F g^{-1} at a current density of 1.0 A g^{-1} and an impressive capacitance as high as 764 F g^{-1} can be delivered even at a current density of 20 A g^{-1} . About 72% of the capacitance for CoS nanobubble cages is retained when the current density increases from 1.0 to 20 A g^{-1} , revealing excellent rate capability. Compared with CoS nanobubble cages, the CoS cages deliver similar rate capability but much lower specific capacitance. Furthermore, the electrochemical stability is evaluated at a current density of 10 A g^{-1} by repeated charging and discharging for 12500 cycles. As shown in Figure 4c, the CoS nanobubble cages manifest exceptional cycling stability and deliver 92.5 % of its initial capacitance after 12500 cycles. On the other hand, the CoS cages show a capacitance loss of 13.7 % over 12500 cycles. After cycling, the CoS nanobubble cages retain their complex structure and chemical composition (Figure S15, see SI). Overall, the electrochemical properties of the CoS nanobubble cages are superior to those of many previously reported cobalt sulfide-based electrode materials.^[3, 9, 34-36]

In summary, a dual-template approach is developed to prepare CoS nanobubble cages by using $\text{TiO}_2/\text{HDA}@\text{ZIF-67}$ composites as templates. A key feature of this new strategy is that each Co-based ZIF-67 polyhedron serves as the host for the effective encapsulation of many TiO_2/HDA nanospheres. These nanoparticles-in-MOF hybrid structures can be easily converted into complex

hierarchically structured cages consisting of separated CoS nanobubbles in the shell. The as-prepared CoS nanobubble cages exhibit remarkable electrochemical performance for hybrid supercapacitors compared with simple CoS cages derived from ZIF-67. The enhanced electrochemical properties might be mainly attributed to the unique structure of the obtained hierarchically structured materials. This strategy can be easily extended to synthesize other MOF-based hybrid structures and may offer a new way for developing highly efficient MOFs-derived functional materials for different energy-related applications.

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Figures captions

Figure 1. Schematic illustration of the controlled encapsulation of TiO_2/HDA nanospheres in each ZIF-67 crystal (I) and its subsequent conversion to CoS nanobubble cage by a sulfidation treatment (II).

Figure 2. FESEM (a,b) and TEM (c,d) images of $\text{TiO}_2/\text{HDA}@\text{ZIF-67}$ particles.

Figure 3. FESEM (a-c) and TEM (d-f) images of CoS nanobubble cages.

Figure 4. Comparative electrochemical properties of CoS nanobubble cages and CoS cages. (a) Cyclic voltammetry curves at a sweep rate of 2.0 mV s^{-1} , (b) specific capacitance as a function of current density, and (c) cycling performance at a current density of 10 A g^{-1} .

for Table of Content Entry

A “nanoparticles-in-MOF” dual-template method is developed to synthesize CoS nanobubble cages. With the structural advantages, these unique CoS nanobubble cages exhibit enhanced electrochemical performance as an electrode material for hybrid supercapacitors.