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# Unusual $CoS_2$ ellipsoids with anisotropic tube-like cavities and their application in supercapacitors†

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**Unusual $CoS_2$ ellipsoids with anisotropic tube-like cavities have been synthesized from the simultaneous thermal decomposition and sulfidation of a preformed cobalt carbonate precursor. The as-prepared $CoS_2$ ellipsoids show interesting supercapacitive properties with high capacitance and good cycling performance.**

Porous functional nanomaterials are of great importance in a wide range of fields, including catalysis, separation, and electrochemical devices.[1–6] The desirable porous structure provides high surface area of the solid material, facilitates diffusion of foreign substances throughout the bulk, and thus improves the performance in various applications. Many strategies have been employed to prepare materials with different porous structures and cavities. For example, organic surfactants have been extensively used as ''soft templates'' to generate ordered mesoporous silica materials,[4] and such mesoporous silica materials could be further utilized as ''hard templates'' to synthesize other porous functional materials *via* nanocasting.[6] However, one drawback of hard template assisted approaches is the tedious procedure that normally leads to additional cost. Meanwhile, novel strategies for the preparation of porous materials from pre-formed solid materials have received much attention in recent years.[7–12] Specifically, metal containing precursors (*e.g.*, metal carbonate/hydroxide/nitrate *etc.*) are first prepared and readily transformed to the corresponding metal oxides with porous structures through procedures such as thermal decomposition and chemical etching. Very recently, we have applied manganese carbonate microsized particles to fabricate complex metal oxide (*e.g.*, $LiNi_{0.5}Mn_{1.5}O_4$) nanostructures with hollow interiors and porous shells.[13] Nevertheless, the transformation process typically leads to the formation of disordered but uniformly distributed pores. Therefore, creating novel porous structures *via* this simple approach remains largely unexplored. In addition, most of the studies so far are still limited to metal oxides as the target products.

Here, we demonstrate the synthesis of microsized $CoS_2$ ellipsoids with unusual anisotropic tube-like cavities *via* a facile sulfidation approach. Many efforts have been made for the synthesis of diverse transition-metal sulfides, owing to their unique physicochemical properties and widespread applications.[14–20] However, the lack of well-established methods makes the synthesis of porous or nanostructured metal sulfides challenging.[21–25] In the synthesis approach presented here, we use pre-formed $CoCO_3$ ellipsoids as the precursor, followed by a simultaneous decomposition and sulfidation process in $H_2S$ gas flow. Unlike typical metal oxides obtained from decomposition of carbonates/hydroxides, in which the nanopores are uniformly distributed on the surface or throughout the bulk of the materials,[11–13] the as-formed $CoS_2$ ellipsoids possess unique tube-like cavities oriented from the center to the surface with openings on the two ends of the ellipsoidal particles. To the best of our knowledge, microparticles with such anisotropically oriented and distributed cavities have not been reported before. Further electrochemical evaluations reveal that these $CoS_2$ ellipsoids manifest attractive supercapacitive performance, which might be attributed to the intrinsic properties of cobalt disulfide and the unique porous structure.

To fabricate porous $CoS_2$ ellipsoids, we first synthesized ellipsoidal $CoCO_3$ microparticles as the precursor using a one-pot solvothermal method previously developed by us with minor modifications (detailed experimental process in ESI†).[12] The crystallographic phase of the precursor was confirmed by powder X-ray diffraction (XRD) analysis to be pure $CoCO_3$ (JCPDS no. 11-0692) with high crystallinity (Fig. S1†). The uniform ellipsoidal shape of the microparticles is revealed by field-emission scanning electron microscopy (FESEM) with slightly rough surface (Fig. S2a, b†). The size of the $CoCO_3$ ellipsoids is typically 3–4 μm in length and about 2 μm in width. Under transmission electron microscopy (TEM) observation (Fig. S2c, d†), these $CoCO_3$ ellipsoids show dense solid texture without discernible porosity. Metal carbonates are usually unstable and easily decomposed into metal oxides at elevated temperatures. To study the decomposition behavior of the $CoCO_3$ precursor, we performed thermogravimetric analysis (TGA) in $N_2$ flow (Fig. S3†). A significant weight loss of about 36 wt% at around 350 °C corresponds to the thermal decomposition of cobalt carbonate into cobalt oxide. Hence, the transformation of $CoCO_3$ into cobalt sulfide was performed at 350 °C, during which the decomposition and sulfidation processes are expected to take place simultaneously.

Fig. 1 displays the XRD pattern of the as-synthesized product. All of the peaks in the pattern are sharp and can be

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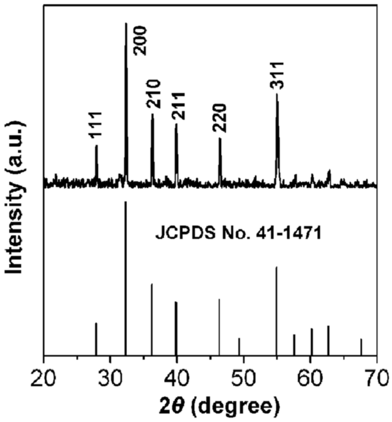

**Fig. 1** XRD pattern of $CoS_2$ ellipsoids with anisotropic tube-like cavities.

unambiguously assigned to $CoS_2$ (JCPDS no. 41-1471), indicating the high phase purity and crystallinity of the as-prepared product. The morphology of the as-prepared $CoS_2$ sample was studied by FESEM as shown in Fig. 2a. The ellipsoidal shape and size of the precursor microparticles are perfectly retained after transformation to the $CoS_2$ phase. A typical magnified FESEM image (Fig. 2b) reveals a very interesting feature of the $CoS_2$ ellipsoids, which is not found in the $CoCO_3$ precursor microparticles. It can be clearly observed that many openings with size of tens of nanometers are located at the two ends of the $CoS_2$ ellipsoids, resulting in much rougher and porous surface in regions with high curvature. To elucidate this unusual structural feature, TEM observation was performed as shown in Fig. 2c and d. Tube-like cavities oriented from the center to the surface can be identified in the ellipsoidal particles, and the openings of the cavities correspond to the nanopores observed in the FESEM images. In agreement with the FESEM observation, the tube-like cavities are distributed around the two ends of the ellipsoidal particles, whereas the non-uniform contrast in the middle region suggests the possible presence of irregular pores. As a result, the solid particles become less dense, as also indicated by the improved transparency under TEM observation. The large particle size and the unique porous structure lead to a limited BET specific surface area of about 17 $m^2 g^{-1}$ (nitrogen adsorption/desorption isotherm shown in Fig. S4†).

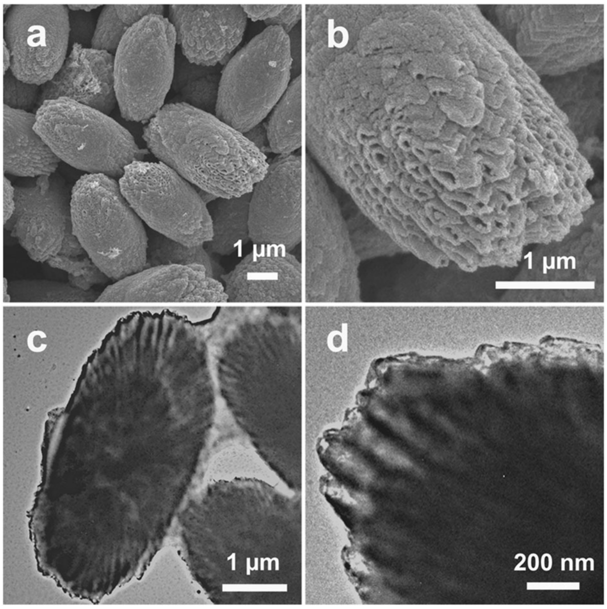

**Fig. 2** (a, b) FESEM and (c, d) TEM images of $CoS_2$ ellipsoids with anisotropic tube-like cavities.

Our previous study shows that direct thermal decomposition of similar $CoCO_3$ microparticles in air results in the formation of $Co_3O_4$ ellipsoids with homogeneously distributed nanopores, which is consistent with other reported porous metal oxides from carbonates/hydroxides.[12] Therefore, the apparent difference between the porous structures of the $Co_3O_4$ and $CoS_2$ ellipsoids, which are from the same precursor particles, suggests that the $H_2S$ gas sulfidation process plays a crucial role in the formation of the anisotropic tube-like cavities. Although the exact mechanism and formation process are still under investigation, we postulate that the $H_2S$ gas might have different reactivity on ellipsoid surfaces with different curvature. Hence, the anisotropic sulfidation on different parts of the surface leads to the formation of anisotropic cavities at the two ends of the ellipsoids.

The family of cobalt sulfides, comprising of many compounds such as CoS, $CoS_2$, $Co_3S_4$ and $Co_{1-x}S$, has been studied as electrode materials for supercapacitors and lithium-ion batteries.[26–32] However, the lack of desirable nanostructures and their intrinsic instability might undermine their performance. In this work, we anticipate that the unique nanostructure of our $CoS_2$ ellipsoids with anisotropic tube-like cavities would benefit their performance in electrochemical applications. Thus, we investigated the electrochemical properties of these porous $CoS_2$ ellipsoids as an electrode for supercapacitors. Typical cyclic voltammograms (CV) of $CoS_2$ ellipsoids in 2 M KOH aqueous electrolyte at various scan rates are shown in Fig. 3a. The shape of the CV curves suggests typical pseudocapacitive characteristics, in which the redox peaks are in general agreement with those of reported cobalt sulfides and oxides.[12,26,28,29] Thus the electrochemical capacitance of $CoS_2$ ellipsoids is attributed to a quasi-reversible electron transfer process that mainly involves the $Co^{2+}/Co^{3+}$ redox couple, and probably mediated by $OH^-$ ions in the alkaline electrolyte as in the case of CoS.[27,28] Compared with the negligible current signal from Ni foam (Fig. S5†), one can safely confirm that the pseudocapacitance indeed comes from the porous $CoS_2$ ellipsoids.

To evaluate the specific capacitance and cycling stability, the $CoS_2$ ellipsoid electrode was galvanostatically charged/discharged within a voltage window of $-0.1$ to 0.4 V *vs.* saturated calomel electrode (SCE) reference electrode in the same alkaline electrolyte. Fig. 3b shows representative charge/discharge curves at various current densities. Consistent with the CV results, the plateaus in the charge/discharge curves indicate the existence of Faradaic processes. The specific capacitance is then simply calculated according to the following equation: $C = I\Delta t/(m\Delta V)$,[12] where $C$ (F $g^{-1}$) is the specific capacitance, $I$ (mA) is the discharge current, $\Delta t$ (s) is the discharge time, $\Delta V$ ($V$) is the potential change during discharge, and $m$ (mg) is the mass of the active material (*i.e.*, $CoS_2$ ellipsoids). On the basis of the charge/discharge profiles shown in Fig. 3b, the specific capacitance of the $CoS_2$ sample is determined to be 1040, 980, 965, 750 and 224 F $g^{-1}$ at 0.5, 1, 2.5, 5 and 10 A $g^{-1}$.

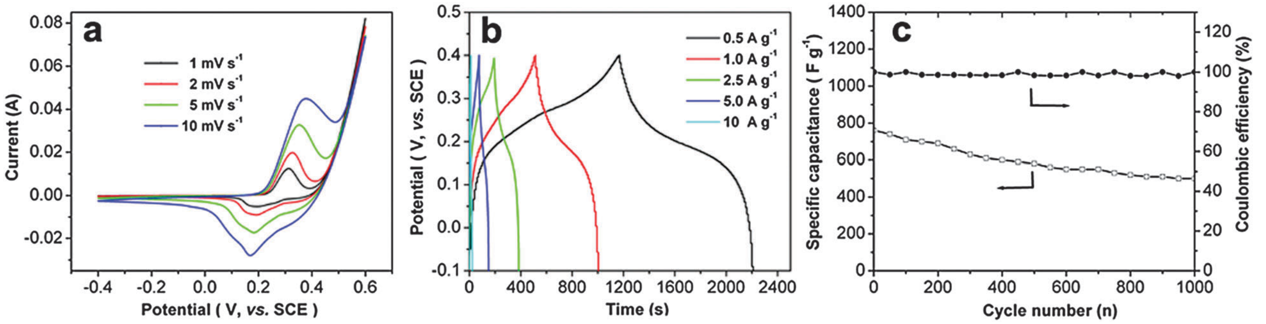

**Fig. 3** (a) Cyclic voltammograms at various scan rates, (b) galvanostatic charge and discharge curves at various current densities, (c) specific capacitance and coulombic efficiency *vs.* cycle number at a current density of 5.0 A $g^{-1}$.

These values of specific capacitance are considered very high for pseudocapacitive materials, especially in view of the relatively low BET surface area ($\sim$17 $m^2$ $g^{-1}$). The good performance of the porous $CoS_2$ ellipsoids as an electrode material for supercapacitors might be attributed to the novel anisotropic cavities that efficiently facilitate the infiltration of electrolyte and also provide more active surface for fast redox reactions. The capacitance retention and Coulombic efficiency upon prolonged cycling are evaluated at constant current densities of 5 and 2.5 A $g^{-1}$ (Fig. 3c and S6†). After 1000 cycles, about 66 and 44% of the initial specific capacitance can be retained, respectively. Meanwhile, a coulombic efficiency of almost 100% during the whole cycling indicates the excellent reversibility of pseudocapacitive reactions in the $CoS_2$ ellipsoids.

In summary, we report the synthesis of porous $CoS_2$ ellipsoids from the simultaneous thermal decomposition and sulfidation of preformed $CoCO_3$ ellipsoidal microparticles. The as-prepared $CoS_2$ ellipsoids possess unusual tube-like cavities that are oriented from the center to the surface and the openings are distributed on the two ends of the ellipsoids. Such anisotropic cavities will not only facilitate the infiltration of electrolyte but also provide more active surface when the $CoS_2$ ellipsoids are evaluated as electrode materials for supercapacitors. Benefiting from the unique porous structure, the $CoS_2$ ellipsoids show high pseudocapacitance and good cycling performance. We anticipate that the facile approach presented in this work could be extended to fabricate other metal sulfide materials with novel nanostructures.

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