Supporting Information for

## Large-scale Co<sub>9</sub>S<sub>8</sub>@C hybrids with tunable carbon thickness for high-rate and long-term performance of aqueous batteries

Cuihua An,<sup>a,b</sup> Mengying Wang,<sup>b</sup> Weiqin Li,<sup>b</sup> Li Xu,<sup>c\*</sup> Yijing Wang<sup>b\*</sup>

a Tianjin Key Laboratory of Advanced Functional Porous Materials, Institute for New Energy Material & Low-Carbon Technologies, School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300384, P.R. China

b Key Laboratory of Advanced Energy Materials Chemistry (MOE), College of Chemistry, Nankai University, Tianjin 300071, P.R. China

c Global Energy Interconnection Research Institute Co., LTD, P.R. China

E-mail: wangyj@nankai.edu.cn and sinoxuly@foxmail.com



Figure S1 XRD patterns of the obtained products with various proportions of Cobalt and sulfur powder.

The XRD patterns from 1:1 to 1:4 are almost the same, and the diffraction peaks can be assigned to amorphous carbon,  $Co_9S_8$  and metal cobalt, indicating that the amount of the sulfur powder is not enough to react with the Co-NA precursor. When increasing the ratio to 1:5, the diffraction peaks of metal cobalt disappear and pure  $Co_9S_8@C$  are obtained.



Figure S2 SEM images of the H0 (a), H1 (b), H2 (c) and H3 (d) samples.

As shown in Fig.S2, they all exhibit one-dimensional (1D) nanorod structures. What these four materials have in common is that the surface of the 1D nanorod is rough and the 1D nanorods are assembled by incalculable nanoparticles. One of the most basic differences is that their diameters and the sizes of the nanoparticles. Specifically, the diameters of H0 and H1 are almost the same, which is around 300 nm. While the structures of H2 and H3 are coarsened in some degree and their diameters are about 700 nm, about twice as much as the two formers. Moreover, there are some mussy bulks in H2 and H3 materials except for the 1D nanorod structure, which is due to the decreased viscosity of the mixed solvent with the increasing  $H_2O$  content.



Figure S3 The histogram statistics of the  $Co_9S_8$  core in H0 (a), H1 (b), H2 (c) and H3

(d) samples.



Figure S4 TG curves of the H0 (a), H1 (b), H2 (c) and H3 (d) samples.

As displayed in Fig. S4, there is an obvious weight loss and the weight loss curves gradually stabilize until about 480 °C for these four samples. And the amount of the weight loss for these four samples are 14.7%, 10.2%, 6.8% and 4.5%, respectively, which is comparative with the calculated results from the ICP-OES (14.6% for H0, 10.2% for H1, 6.6% for H2 and 4.3% for H3).



Figure S5  $N_2$  adsorption/desorption isotherms (a) and the pore size distributions (b) of H1 materials.

Table S1 The specific surface area and pore size distributions of the four Co<sub>9</sub>S<sub>8</sub>@C samples

Sample	BET $(m^2 g^{-1})$	Pore Size Distribution (nm)
H0	87.2	17.8
H1	72.1	17.7
H2	58.4	16.9
Н3	42.3	16.5



Figure S6 SEM (a-b) and TEM (c-d) images of the H1 electrode after 100 cycles and

200 cycles.