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Supporting Information

Hierarchical $Cu_{2-X}Se$ nanotubes constructed by two-unit-cell-thick nanosheets: room-temperature synthesis and promoted electrocatalytic activity towards polysulfides

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Details of experiments:

Preparation of Cubic Cu_2O: Cubic Cu_2O nanoparticles were synthesized by a method according to the previous report.[1] 0.20 g PVP (polyvinylpyrrolidone) was dissolved into $CuSO_4$ aqueous solution (100.0 ml, 0.01M) under magnetic stirring at room temperature, followed by the addition of NaOH aqueous solution (25.0 ml 1.50 M),stirring for two minutes. And then, 25.0 ml 0.10 M ascorbic acid solution was added into the mixture and stirred for another 15 minutes. The precipitation were washed by deionized water and absolute ethanol for several times, and then dried in a vacuum system.

Preparation of Cubic $Cu_{2-X}Se$： The above Cu_2O powders were followed ultrasonic wave dispersed in 10ml distilled water at room temperature for 10 min. The suspension were added into 20 ml the as prepared selenium solution at room temperature for 30 min. Then the obtained materials were immersed to a 14.4% ammonia solution for 8h. The obtained product was washed with deionized water and absolute ethanol, and dried at ambient temperature under vacuum.

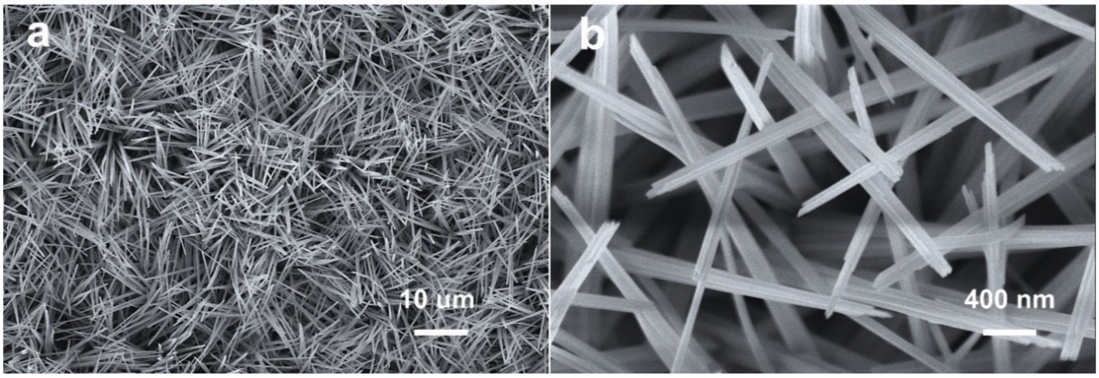

Figure S1. FESEM images: (a, b) the as-prepared $Cu(OH)_2$ nanorod arrays.

The morphology of the as-prepared $Cu(OH)_2$ nanorod arrays is shown in Figure S1. From which one can see that $Cu(OH)_2$ arrays are formed with nanorods standing on copper substrate. The average diameter of $Cu(OH)_2$ nanorods is about 200 nm and the surface morphology is smooth (Figure S1b).

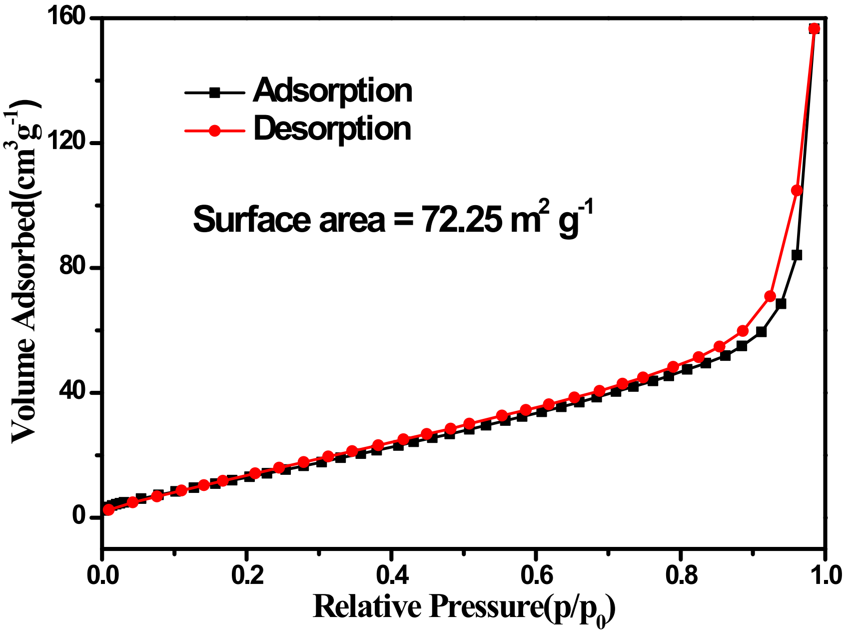

Figure S2. Nitrogen adsorption/desorption isotherms of the as-prepared $Cu_{2-X}Se$.

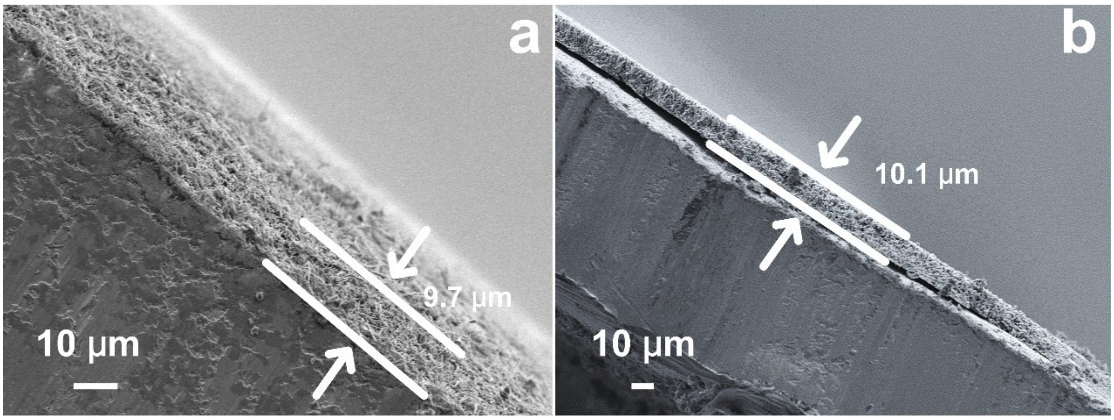

Figure S3. SEM: (a-b) the thickness of $Cu(OH)_2$ and $Cu_{2-X}Se$ films.

As is shown in figure S3a, the thickness of $Cu(OH)_2$ film is about 9.7 μm. After the as-prepared $Cu(OH)_2$ nanorod arrays being immersed in 0.01 M Se^{2-} solution for 30 minutes and following to dissolve $Cu(OH)_2$ cores by dilute ammonia solution, typical $Cu_{2-X}Se$-1 product is obtained. As shown in figure S3b, the thickness of $Cu_{2-X}Se$ film is about 10.1 nm.

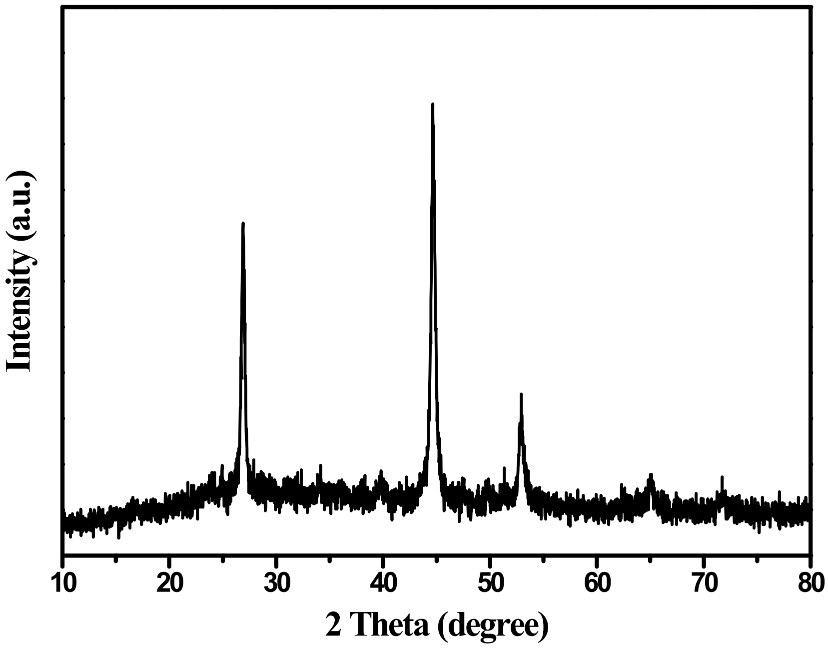

Figure S4. XRD patterns of the the obtained $Cu_{2-X}Se$.

All the diffraction peaks (figure S4) can be indexed to the standard diffractions of cubic $Cu_{2-X}Se$ (JCPDF 6-680).

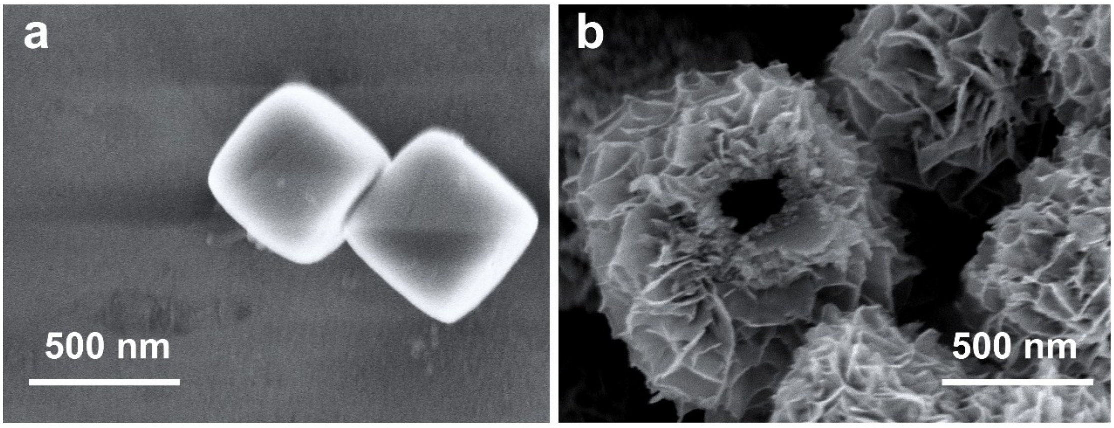

Figure S5. The FE-SEM morphologies of: (a) the as-prepared precursor Cu_2O cube, (b) the obtained $Cu_{2-X}Se$.

As is shown in figure S5a, the average diameter of the cubic Cu_2O is about 400 nm and the surface of the Cu_2O is smooth. Figure S5b shows the average diameter of these hierarchical nanostructures is about 900 nm. What's more, the $Cu_{2\text{-}X}Se$ hierarchical nanostructures were assembled with well-distributed bi-unit-cells thick nanosheets, which is similar with the $Cu_{2\text{-}X}Se$ synthesized by using $Cu(OH)_2$ templates. As a result, the design concept of bi-unit-cells thick nanosheets constructed materials can also be extended to build efficiency functional hierarchical structures with diverse sacrificial templates (such as cubic Cu_2O), which are promising not only for photovoltaic device, but also other applications.

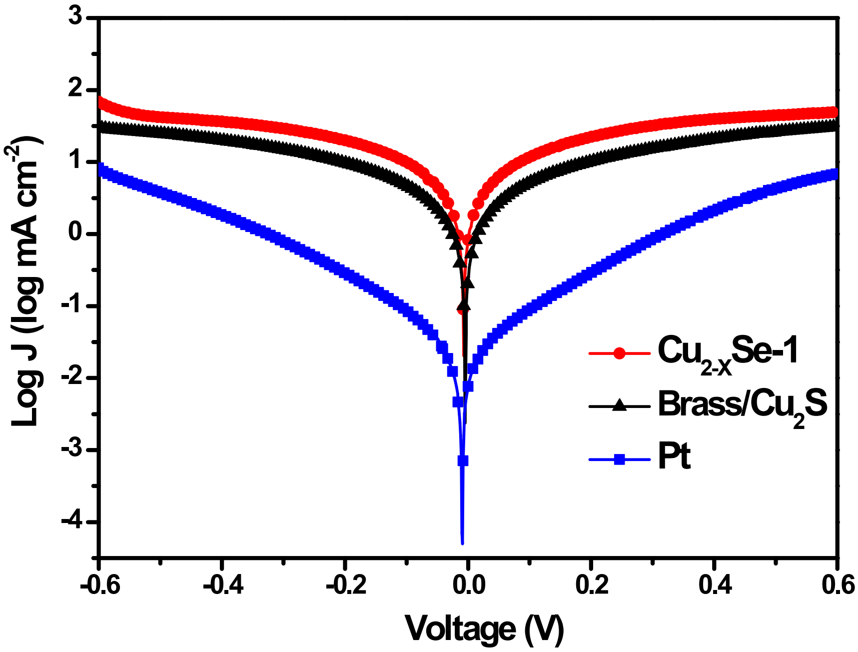

Figure S6. Tafel polarization curves of the CEs.

Figure S6 shows the Tafel curves. The Tafel polarization curves disaplay the logarithmic current density (log J) versus the voltage (V) for the oxidation/reduction of S_n^{2-} to nS^{2-}. The exchange current density (J_0) can be defined as the intercept of the extrapolated linear region of anodic and cathodic branches under the zero voltage. The Tafel polarization curves reveals that the tendency of J_0 value is $Cu_{2\text{-}X}Se$-1＞Cu_2S/Brass＞Pt, indicating the higher exchange current density of $Cu_{2\text{-}X}Se$ electrode. What's more, The J_0 also can be calculated by the equation 1.[2]

$$J_0 = RT / nFR_{CT} \qquad (1)$$

R is the gas constant, T is the temperature, n is the electron number involved in the electrochemical reduction of polysulfide electrolyte, and F is Faraday's constant, and R_{CT} is the value obtained from EIS plots. Therefore, the measured J_0 was in well agreement with the EIS results after calculated in terms of the above equation. The limiting diffusion current density (J_{limit}) obtained from the diffusion zones can evaluate the diffusion of ionic carriers. The Tafel curves showed higher J_{limit} of $Cu_{2-X}Se$-1 CEs than Cu_2S/Brass and Pt CEs from the diffusion zone. Furthermore, diffusion coefficient (D) can be obtained by the equation 2.[2]

$$D = lJ_{limit}/2nFC \qquad (2)$$

l represents the spacer thickness, n is the electron number involved in the polysulfide redox couple, F is Faraday's constant and C is the electrolyte concentration. It's obvious that the $Cu_{2-X}Se$ CE has the largest D value, indicating the fast diffusion velocity of the redox couple in the polysulfide electrolyte, which is beneficial for the electrocatalytic performance. Both of the J_{limit} and D are in accordance with the EIS characters.

Reference

1. H. L. Cao, X. F. Qian, J. T. Zai, J. Yin and Z. K. Zhu, Chem Commun, 2006, 4548-4550.
2. J. W. Xiao, X. W. Zeng, W. Chen, F. Xiao and S. Wang, Chem Commun, 2013, 49, 11734-11736.