Electronic Supplementary Information for
One-pot galvanic formation of ultrathin-shell Sn/CoO_x nanohollows as high performance anode materials in lithium ion batteries

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Experimental General

TEM images and EDS spectra were obtained using a JEOL 2100F unit operated at 200kV. PXRD patterns were obtained using a Rigaku MAX-2200 and filtered Cu-Ka radiation. The XPS spectrum was obtained using a Thermo VG and Monochromatic Al-*Kα* radiation. The ^1H NMR spectrum was recorded with a Varian (300 MHz) spectrometer. Infrared (IR) absorption spectrum was obtained using AVATAR 320 FT-IR spectrometer. Elemental analysis was performed on a CE EA1110 instrument.

Synthetic procedure of the heterobimetallic precursor: The $Ph_3SnCo(CO)_4$ is a known compound and was prepared by the modified method from the literature (A. D. Beveridge, H. C. Clark, *J. Organometal. Chem.* 1968, **11**, 601.) as following. Naphthalene (1.0 g, 7.8 mmol) and sodium (0.18 g, 7.8 mmol) were added to a flame-dried 100 mL one-neck Schlenk flask under argon. Freshly distilled and degassed THF (30 mL) was added into the Schlenk flask. The reaction mixture was stirred overnight at room temperature. Then, $Co_2(CO)_8$ (1.3 g, 3.9 mmol) was added into the Schlenk flask under argon and the reaction mixture was stirred for additional 3 hours. Ph_3SnCl (3.3 g, 8.6 mmol) was added and the reaction mixture was stirred for 2 hours at room temperature. The solution was filtrated through celite. The solvent was then evaporated. The yellow crystalline $Ph_3SnCo(CO)_4$ was obtained by growing single crystals in pentane. The elemental analysis for the obtained $Ph_3Sn\text{-}Co(CO)_4$ crystals showed 50.78 w% for C and, 2.96 w% for H with theoretical values of 50.72 w% for C and 2.90 w% for H, respectively. ^1H NMR peaks of the precursor in $CDCl_3$ solution appeared at 7.60 (m, 6H) and 7.41 (m, 9H) ppm. IR absorption peaks of carbonyl ligands appeared at 2087 (s), 2026 (s), 1997 (vs) cm^{-1}. It should be noted that for the preparation of high-quality hollow materials, the precursor quality should be sufficiently high. The existence of additional tin-containing byproducts such as unreacted Ph_3SnCl in the precursor results in the formation of a massive mixture of materials.

Synthetic procedure of ultrathin shell Sn/CoO_x hollows (US-HS): Oleylamine (5 mL) was added to a 50 mL two-neck Schlenk flask, dried under vacuum at 110 °C for 4 hours and then, heated to 260 °C. $Ph_3SnCo(CO)_4$ (50 mg) was dissolved in well-dried oleyamine (2 mL) and the resultant solution was hot-injected into oleylamine at 260 °C. At this temperature, the reaction mixture was stirred for additional 12 hours and cooled to room temperature. The addition of excess methanol resulted in the formation of black precipitates which were isolated by centrifugation. The solid was washed with methanol several times and dried under vacuum.

Fabrication of electrochemical cells*:* For the preparation of a working electrode, **US-HS** (80 mg), Super P carbon black (10 mg) and polyvinylidene fluoride binder (10 mg) were mixed in N-methylpyrrolidone (NMP). Then, copper foil was coated with this mixture, dried under a vacuum at 120 ^{o}C overnight and heat-treated at 400 ^{o}C for 3 hours under argon. The working electrodes were prepared by cutting the copper electrode coated with **US-HS** into a circular shape with a 1.4 cm diameter. In a glove box filled with argon, electrochemical cells were assembled using coin-type half cells (CR2016 type), Li metal as the counter electrode and 1 M $LiPF_6$ in ethylene carbonate/diethyl carbonate (1:1 v/v) as the electrolyte. The discharge/charge cycle tests were performed using a WBCS3000 automatic battery cycler system.

Figure S1. Diameter distribution diagram of **US-HS** materials.

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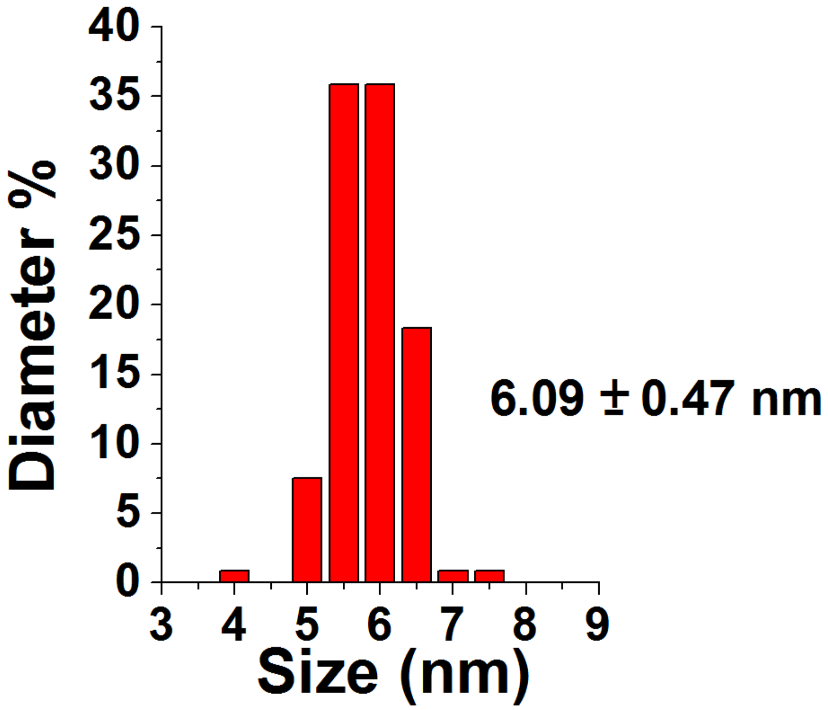


Figure S2. The magnified TEM image of **US-HS** in Fig. 2 in text.

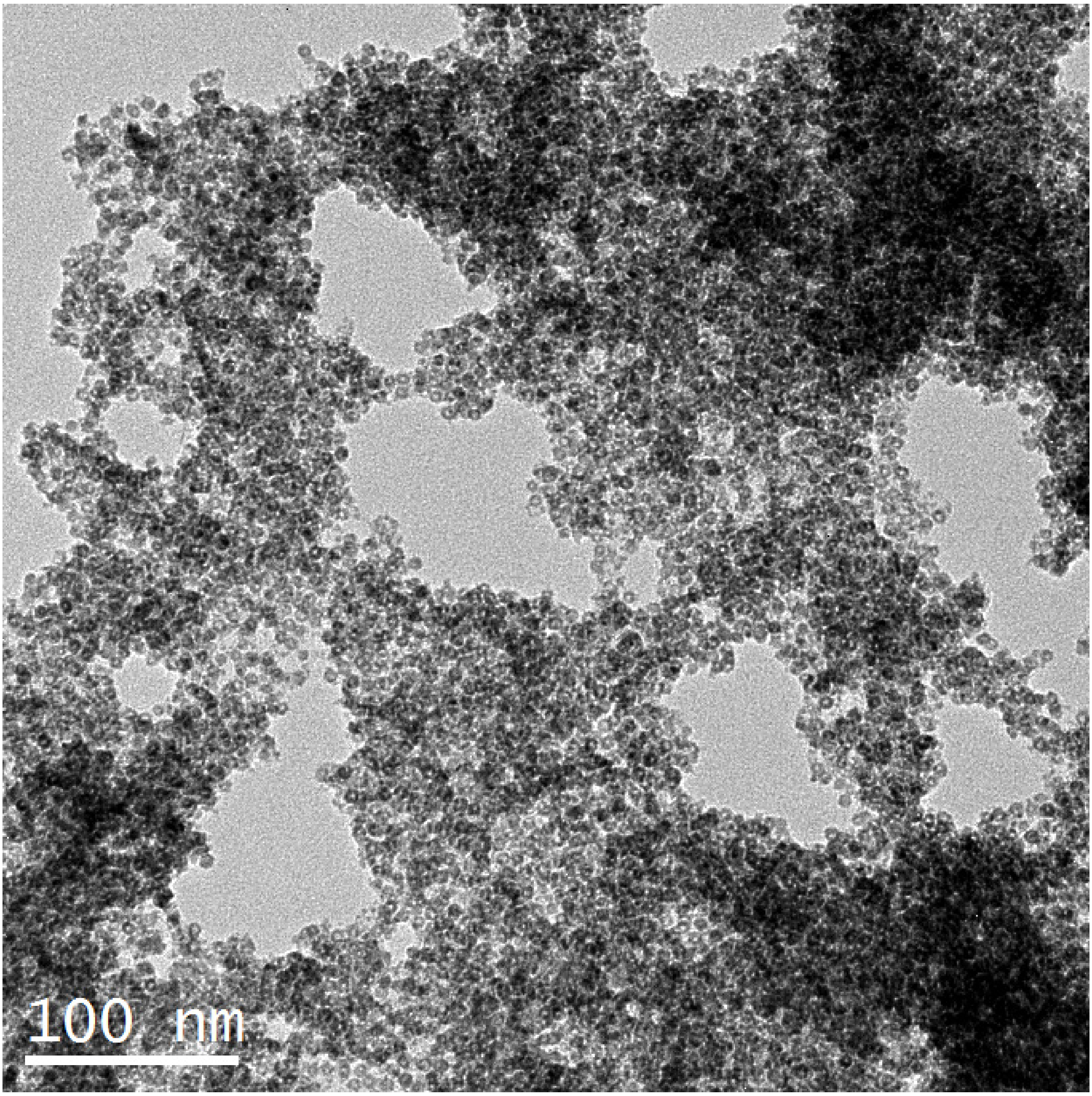


Figure S3. HR-TEM image and ED pattern of **US-HS**.

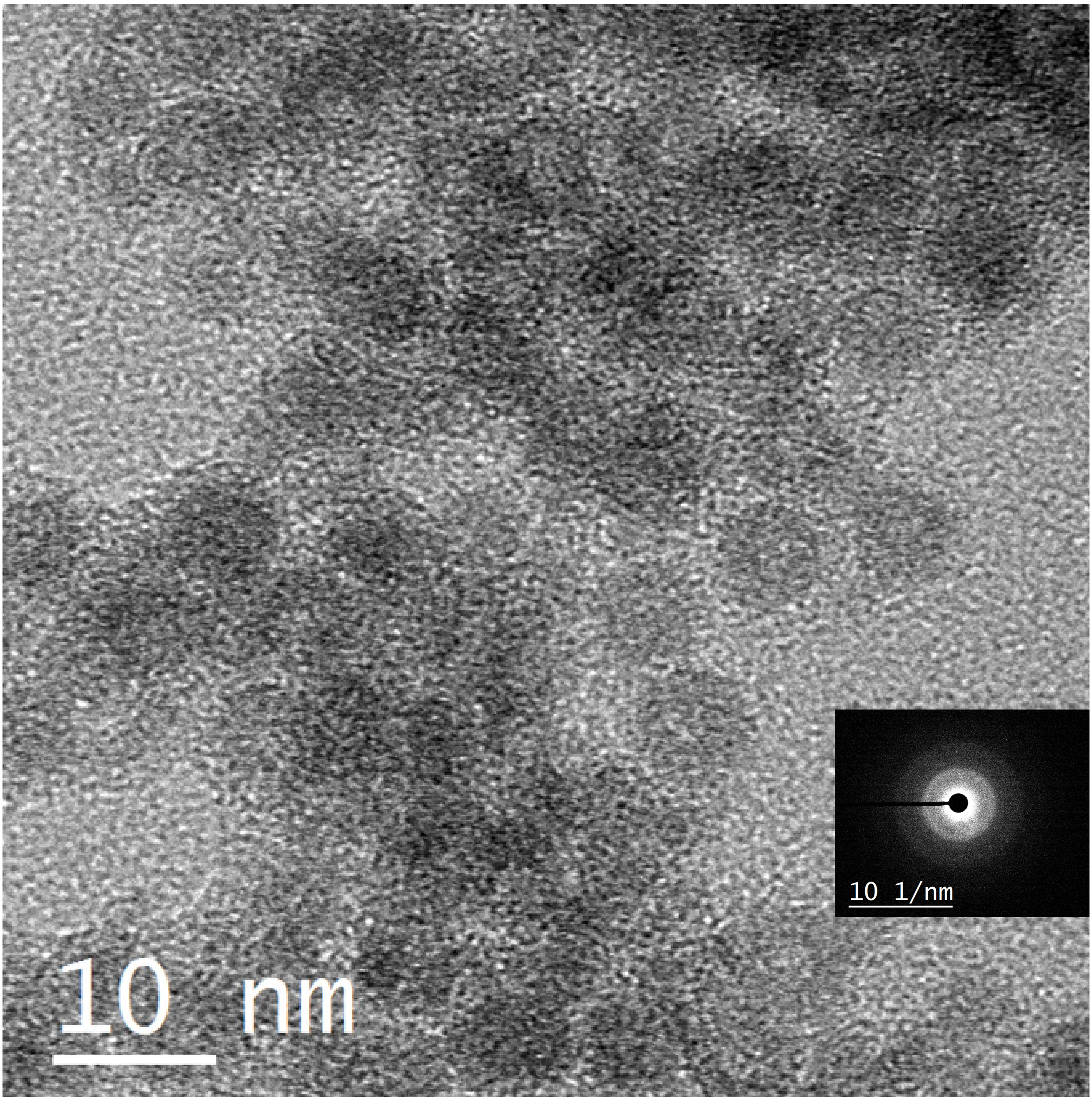


Figure S4. Low magnification TEM image of materials in Fig. 3d in text.

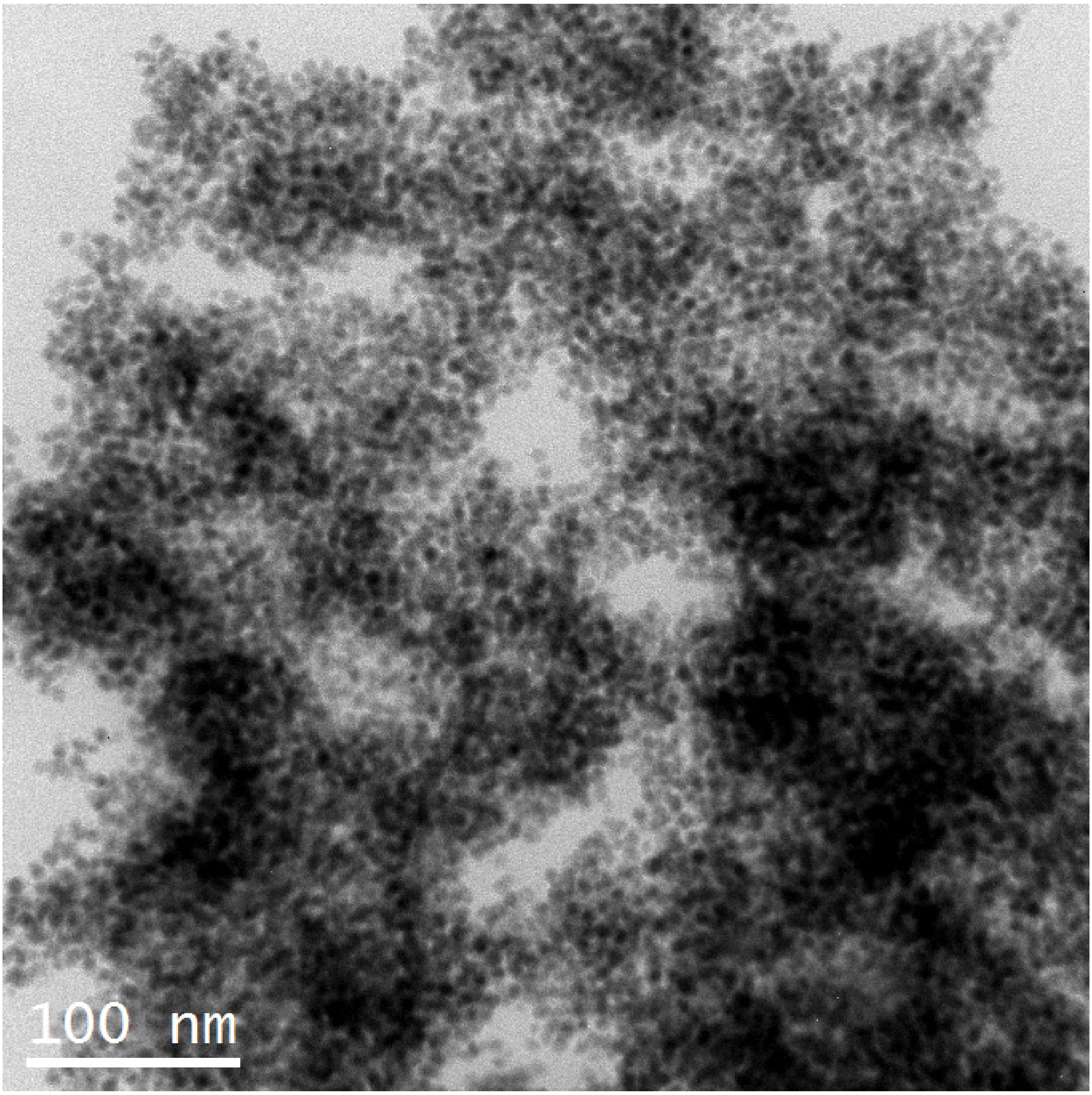
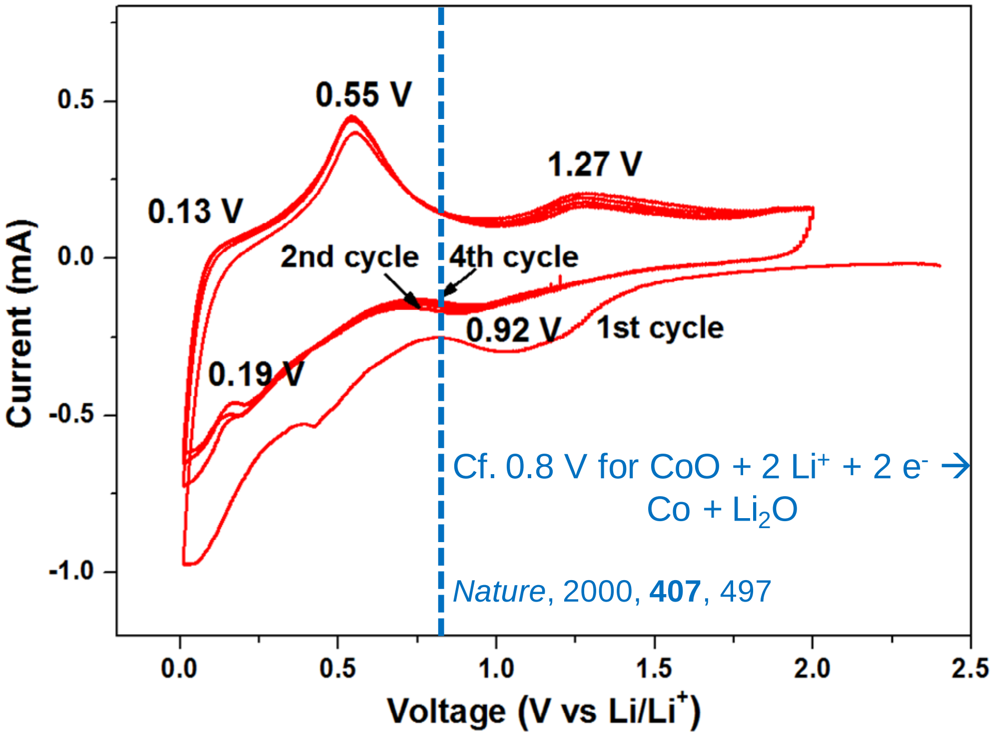
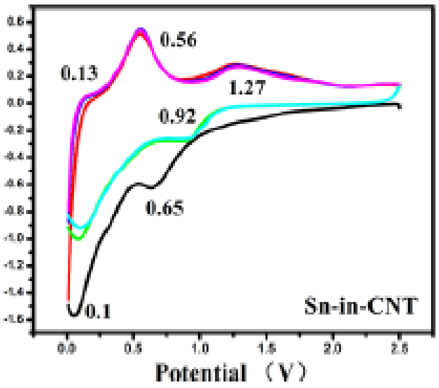


Figure S5. Cyclovoltammogram of electrochemical cell (scan rate = 0.1 mV/s) prepared by **US-HS**.



Cf.



Cyclovoltammogram of zerovalent Sn/C anode mateirals
H. Zhang et al, *J. Phys. Chem. C*, 2012, **116**, 22774
(scan rate = 0.1 mV/s)