Experimental Sections

Materials: Dithizone ($C_{13}H_{12}N_4S$, AR), antimony(III) chloride($SbCl_3$, 99.98%), glucose ($C_6H_{12}O_6$, ≥99.5%) were purchased from Aladdin. Ethylenediamine ($C_2H_8N_2$, 99%) was purchased from Alfa Aesar. Ethanol (99.7%) was obtained from Chengdu Chron Chemicals Co., Ltd. All chemicals were used directly without any further purification.

Synthesis of uniform Sb microspheres: Uniform antimony microspheres were synthesized by hydrothermal method. In a typical synthesis process, 2 mmol of $SbCl_3$ (0.4562 g) and 2 mmol of dithizone (0.5127 g) were dissolved in 37.5 mL of ethylenediamine under stirring for 1 h to form a homogeneous solution. The resultant solution was then transferred into a 50 mL Teflon-lined autoclave and kept at 140°C for 3 days. After cooling to room temperature naturally, the black product was separated by centrifugation and washed with ethanol for several times. Afterwards, the obtained precipitation was dried under vacuum at 60°C for 24 h.

Synthesis of Sb@PA microspheres: 29 mg of Sb microspheres and 116 mg of glucose were dispersed into 10 mL of deionized water with sonication for 10 minutes and then stirred for 1 h. Afterwards, the above solution was transferred into a 50 mL Teflon-lined autoclave and kept at 190°C for 10 h. After cooling to room temperature naturally, the products were collected by centrifugation and washed with ethanol and deionized water for six times, respectively, and dried under vacuum at 60°C overnight.

Synthesis of Sb@C microspheres: In a typical synthesis, 60 mg of the as-synthesized Sb@PA microspheres were annealed at 620°C in an H_2/Ar flow with a heating rate of 5°C min^{-1} for 0.5, 2, 6 and 12 h, respectively.

Materials characterization:

Powder X-ray diffraction was performed on a Rigaku D/MAX RINT-2000 X-Ray diffractometer with Cu Kα (λ=1.54 Å)radiation at a voltage of 40 kV and a current of 40 mA. The morphology and microstructure of the samples were investigated by scanning electron microscopy (JEOL JSM-7500F) and transmission electron microscopy (HITACHI HT7700). Raman spectra of the as-prepared samples were recorded on a Horiba JY LabRAM HR Raman spectrometer. Thermogravimetric analysis (TGA) was performed with a temperature ramp of 10 °C min^{-1} under air flow.

Electrochemical measurements:

The sodium-storage performances of the Sb@C microspheres were examined by 2032 type coin cells in a half-cell configuration. The working electrode were prepared by mixing 70 wt% active materials, 20 wt% carbon black, and 10 wt% carboxymethylcellulose sodium to form a slurry, which was then spread on a copper foil using a blade and dried under vacuum at 60 °C for 12h. The coated copper foil was roll-pressed at 4 MPa and punched into Φ12 mm discs. The typical mass loading of active materials was controlled at 0.8-1.2 mg/cm^{-2}. The electrolyte was a solution of 1M $NaClO_4$ in ethylene carbonate/diethyl carbonate (1:1 by volume) with 5% fluoroethylene carbonate additive. Sodium foils were cut into discs and used as both counter electrode and reference electrode. All the cells were assembled in a glove box with water/oxygen content lower than 0.1 ppm and then tested in LAND CT2001A battery tester (Wuhan LAND Electronic Co., Ltd.) with a voltage range between 0.01 and 2.00 V. Cyclic voltammetry (CV) curves were tested using a Biologic VMP3 electrochemical workstation with a scan rate of 0.1 mV s^{-1}.

Estimation the void ratio of Sb@C microsphere:

As the Sb@C-30min exhibit a core-shell structure, and no void space was observed inside the Sb@C microspheres, the Sb@C-30min can be seemed as a carbon shell completely filled with Sb. In this context, the void space ratio of Sb@C yolk-shell microspheres can be estimated based on the following equation:

$$\frac{(1-\eta_x)\times\varphi_{30min}}{1-\varphi_{30min}+(1-\eta_x)\times\varphi_{30min}}=\varphi_x \qquad \text{(E1)}$$

$$\eta_x=\left(1-\frac{\varphi_x\times(1-\varphi_{30min})}{(1-\varphi_x)\times\varphi_{30min}}\right) \qquad \text{(E2)}$$

Where η_x is the void ratio of sample x. φ_x is the Sb content of sample x. φ_{30min} is the Sb content of sample Sb@C-30min. According to the TGA results, the Sb content in Sb@C-30min, Sb@C-2h, Sb@C-4h and Sb@C-8h is estimated to be 90%, 87%, 70% and 52%, respectively. The void ratio of Sb@C-30min, Sb@C-2h, Sb@C-4h and Sb@C-8h is calculated to be 0%, 23%, 74% and 88%, respectively.

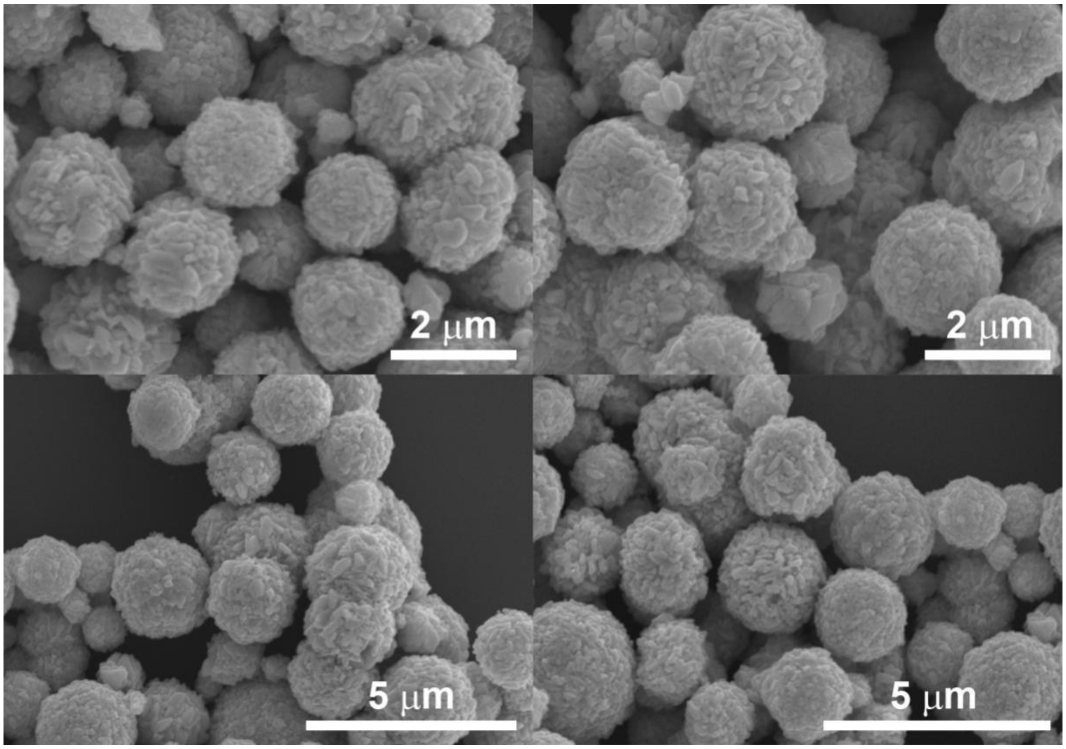

Fig. S1 SEM images of Sb microspheres.

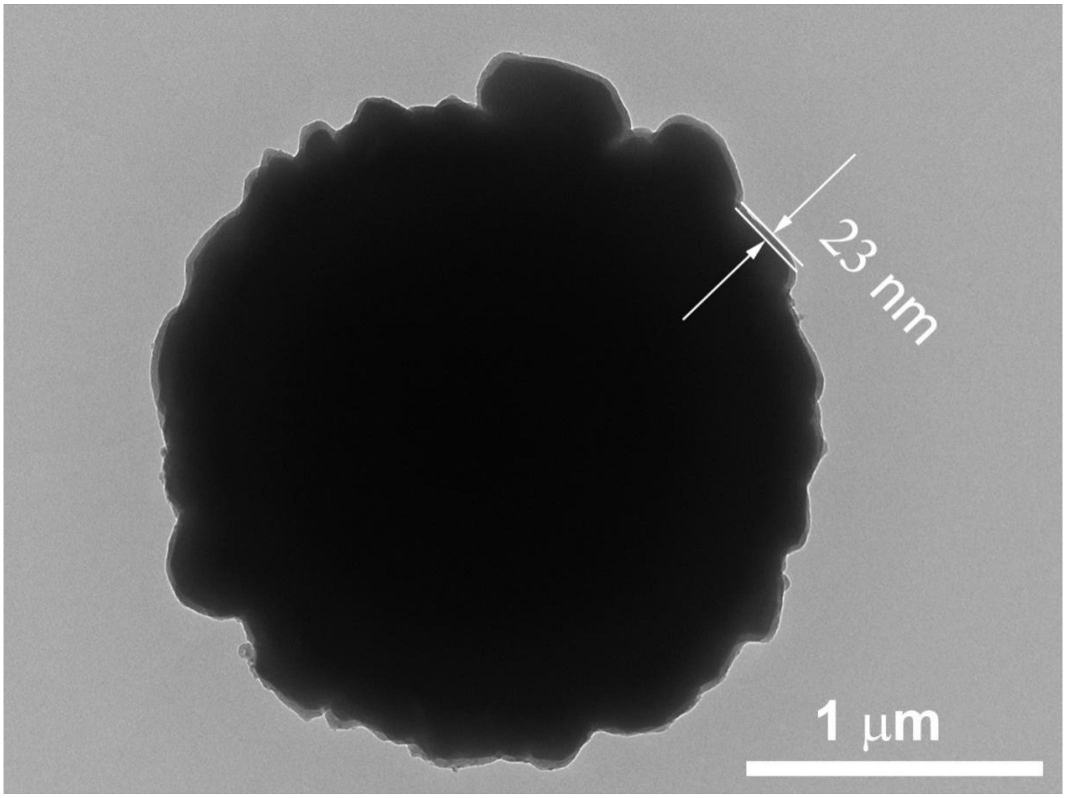

Fig. S2 TEM image of Sb@PA microspheres.

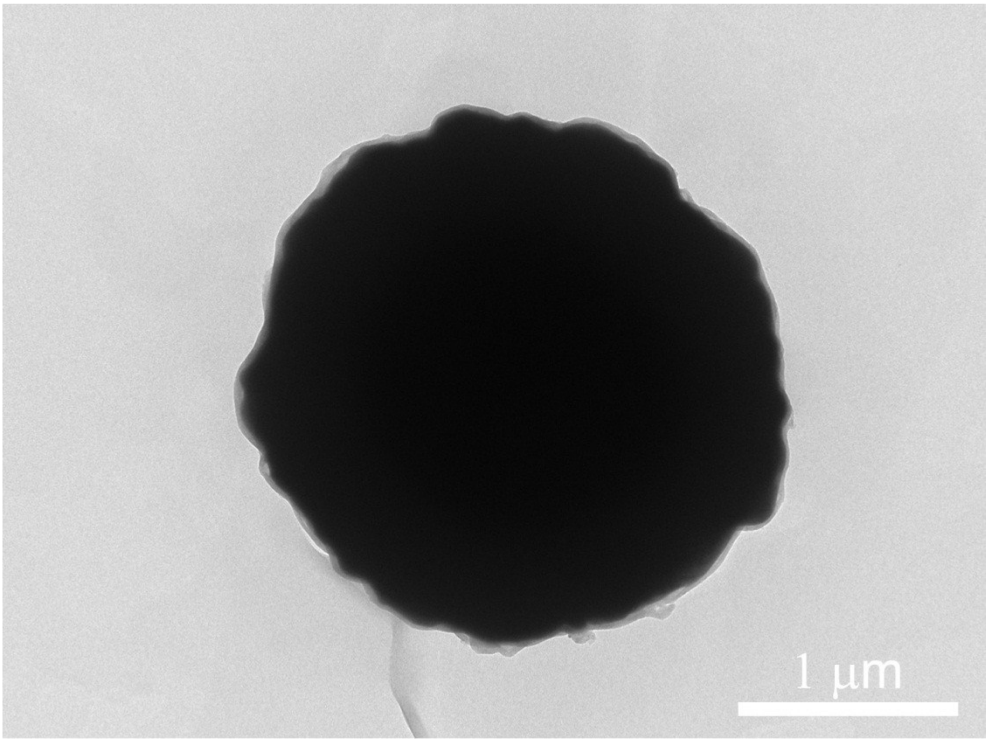

Fig. S3 TEM image of Sb@C-30min.

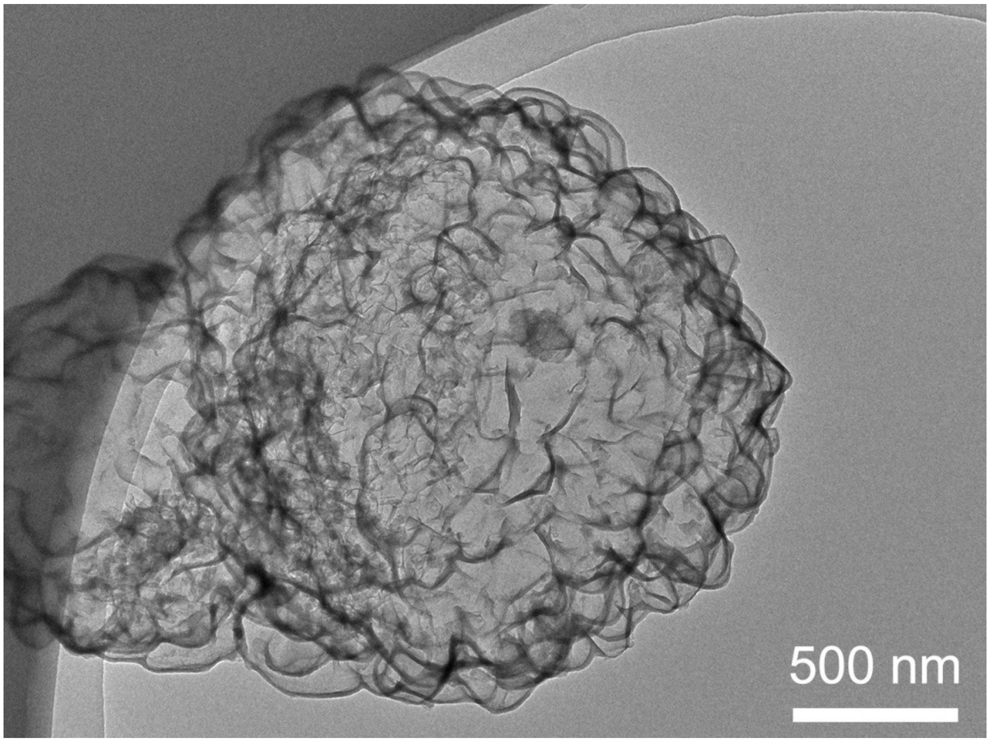

Fig. S4 TEM image of Sb@C-48h.

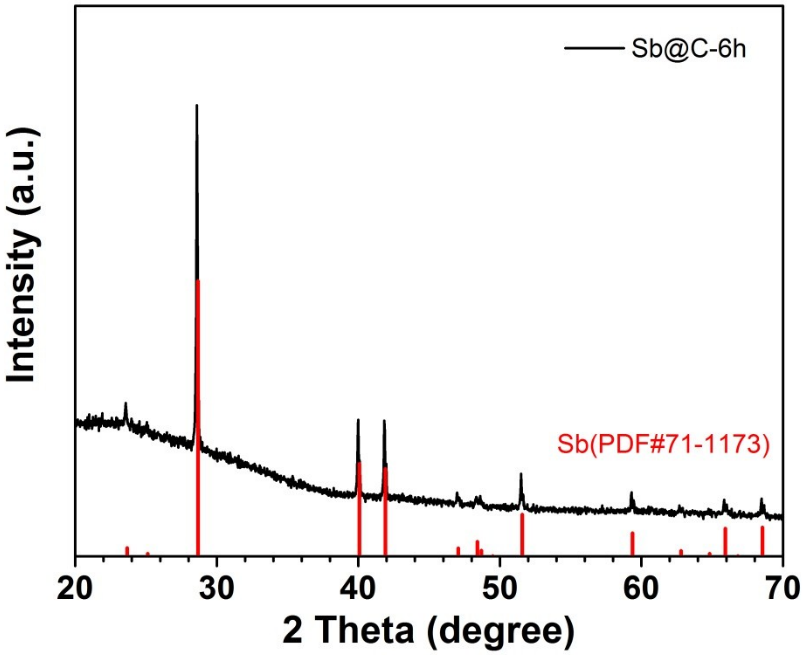

Fig. S5 XRD pattern of Sb@C-6h.

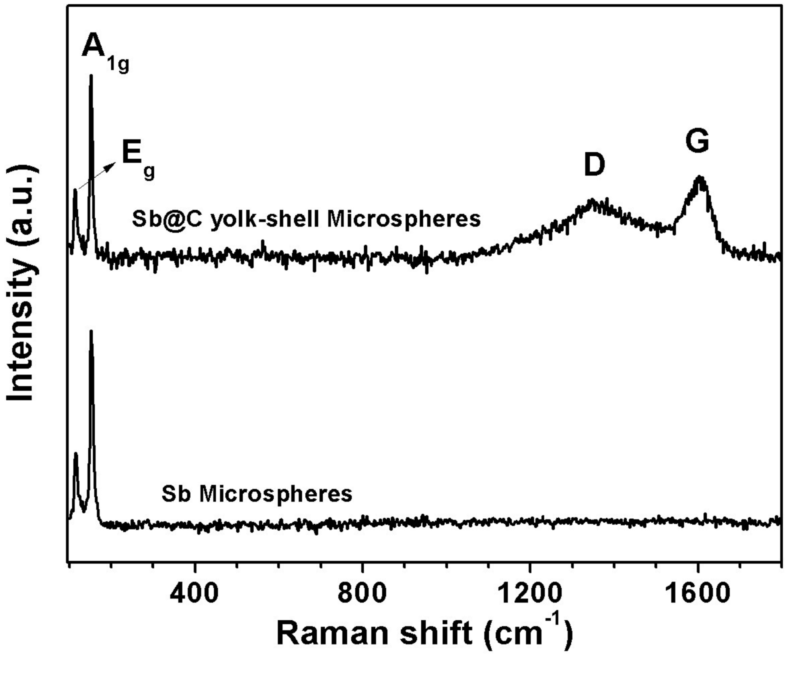

Fig. S6 Raman spectra of Sb microspheres and Sb@C-6h.

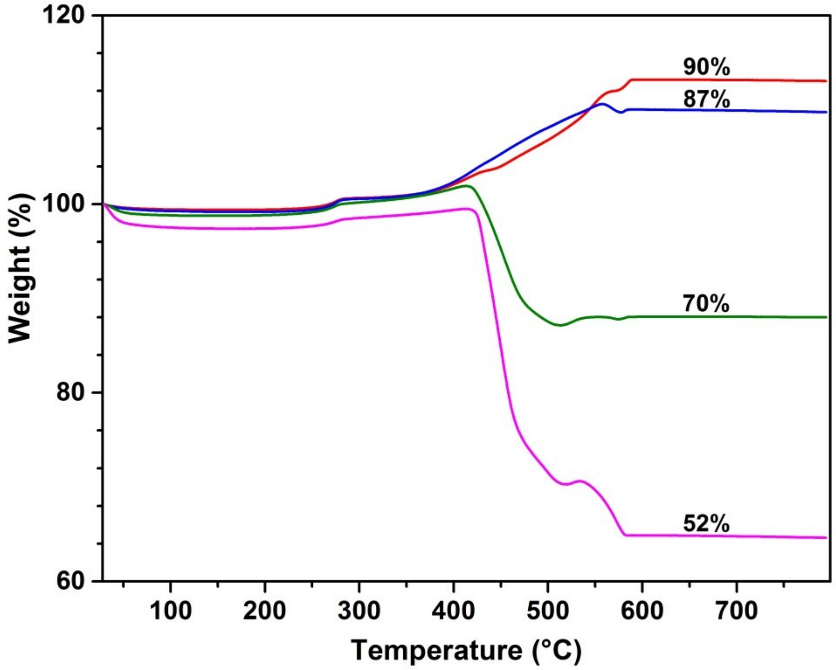

Fig. S7 TGA analysis of Sb@C microspheres at a temperature ramp of 10 °C min^{-1} in air.

The Sb content in the Sb@C microspheres is measured by TGA. The major weight loss between 420 and 570°C can be attributed to the combustion of carbon. when the temperature is above 300°C, metallic Sb will be oxidized to Sb_2O_4. Based on the final weight of Sb_2O_4, the Sb content in the sample can be calculated using the following equation:

$$Sb\ content = \frac{M_{Sb}}{M_{Sb_2O_4}} \times \frac{final\ weight\ of\ Sb_2O_4}{initial\ weight\ of\ Sb@C\ microspheres}$$

Where M_{Sb} is the molecular weight of Sb, $M_{Sb_2O_4}$ is the molucular weight of Sb_2O_4.

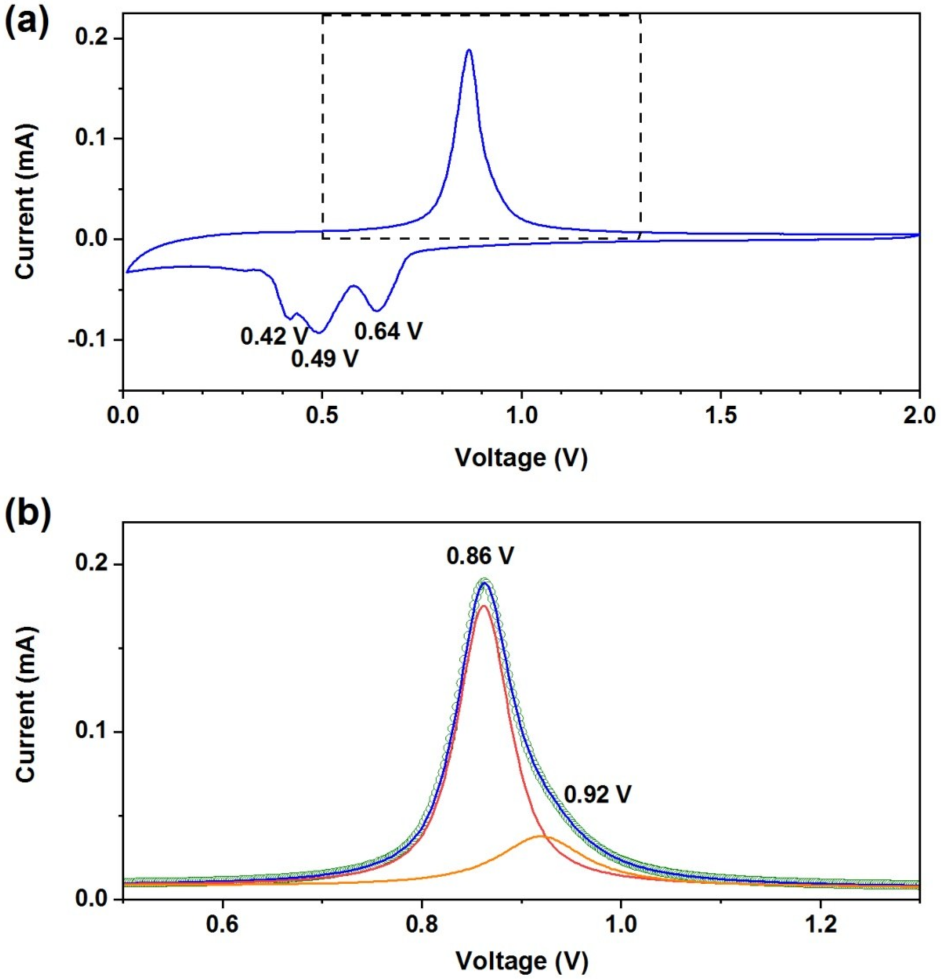

Fig. S8 (a) The second CV cycle of Sb@C-6h; (b) the enlarged anodic peaks of (a).

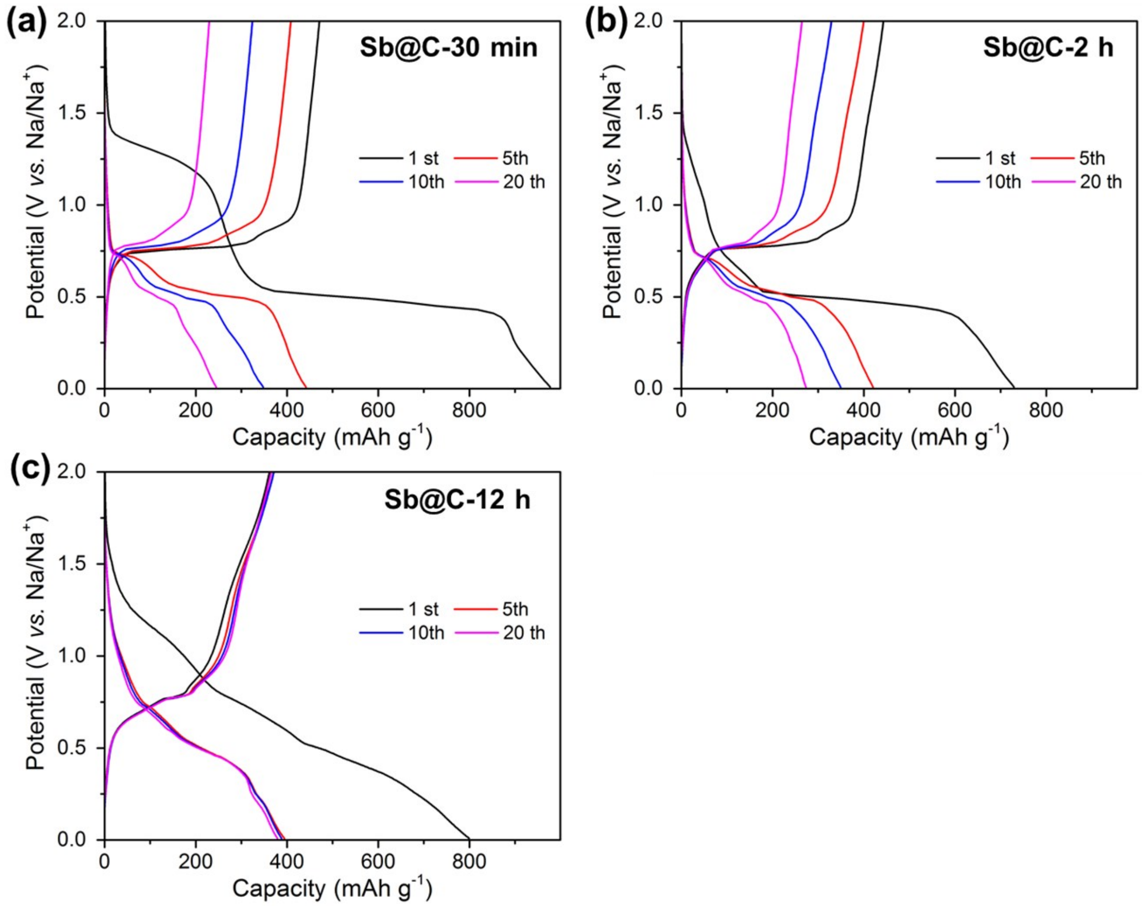

Fig. S9 Galvanostatic charge-discharge profiles of Sb@C-30min, Sb@C-2h and Sb@C-12h at a current density of 100 mA g^{-1}.

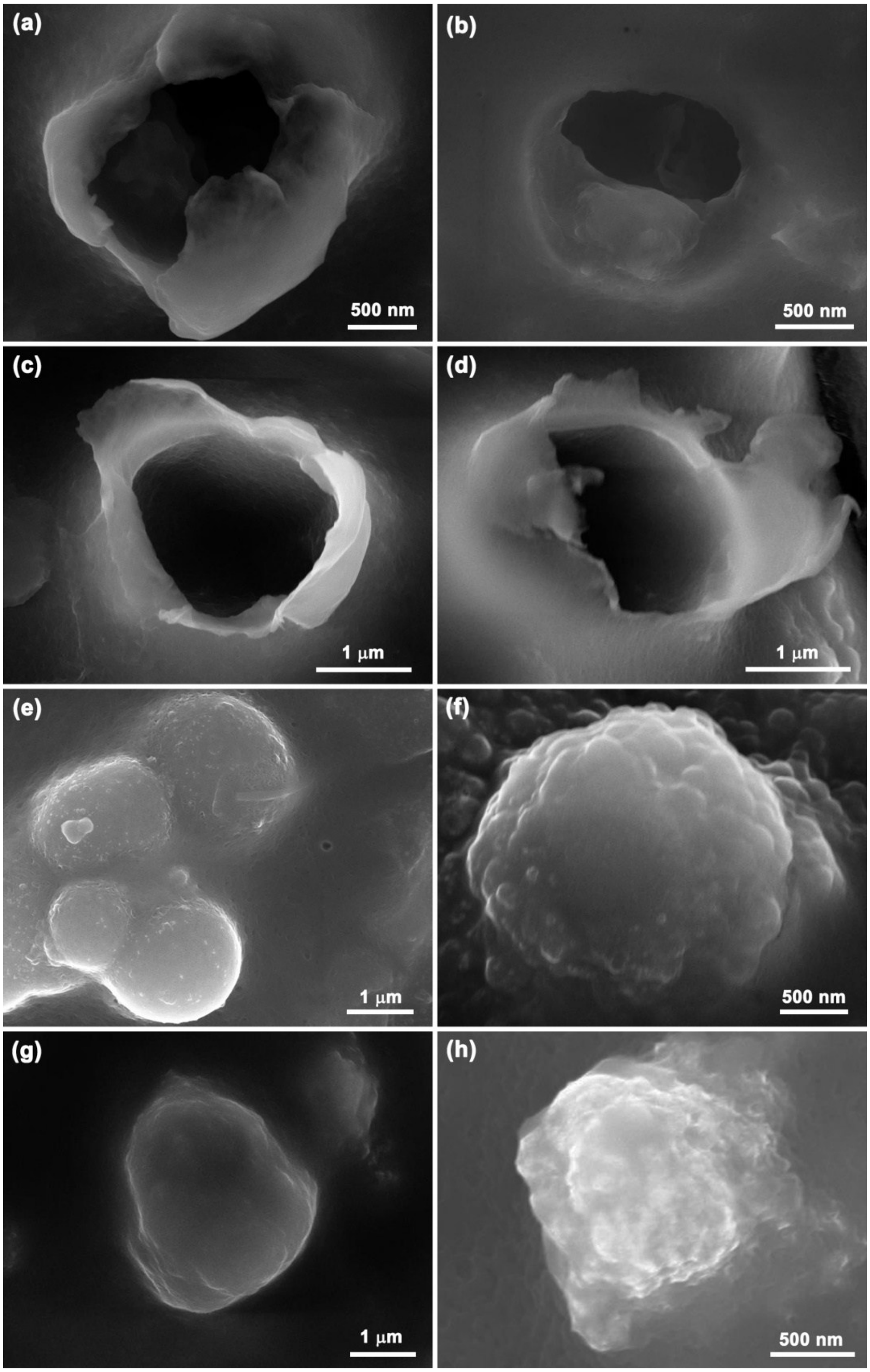

Fig. S10 SEM images of (a,b) Sb@C-30min, (c,d) Sb@C-2h, (e,f) Sb@C-6h, and (g,h) Sb@C-12h after 300 cycles at a current density of 1 A g^{-1}.

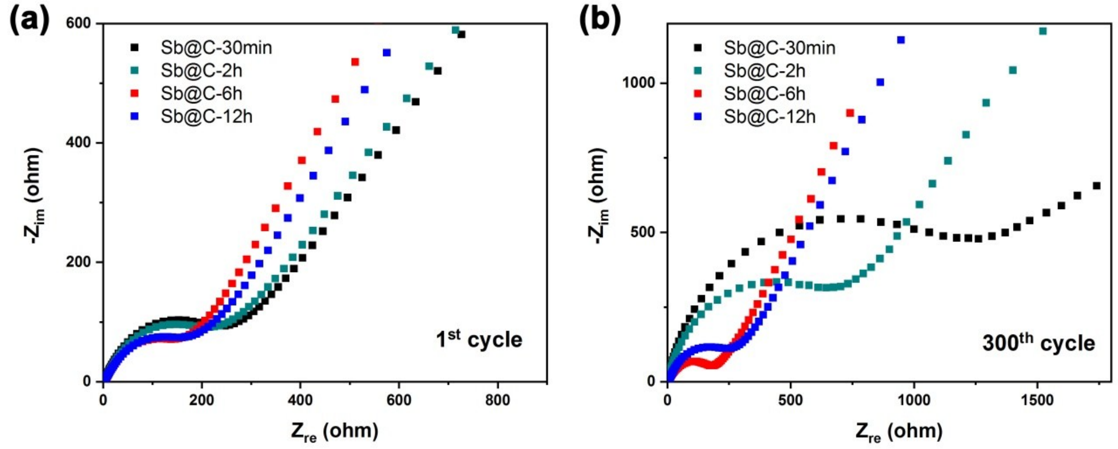

Fig. S11 Nyquist plots of the Sb@C-30min, Sb@C-2h, Sb@C-6h and Sb@C-12h electrodes after (a) 1st cycle and (b) 300th cycle.