

## Supporting Information

# Suppression of Long-Chain Lithium Polysulfides Formation through Selenium-Doped Linear Sulfur Copolymer Cathode for High- Performance Lithium–Organosulfur Batteries

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## Experimental Section

**Reagents and materials.** Selenium powder (Se, A.R. grade), trithiocyanuric acid (TTCA, > 99.5%) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Sulfur powder (S, A.R. grade) was purchased from Tianjin Fuchen Chemical Research Factory. Other organic solvents were purchased from Beijing Chemical Works. All chemicals were used as received without further purification.

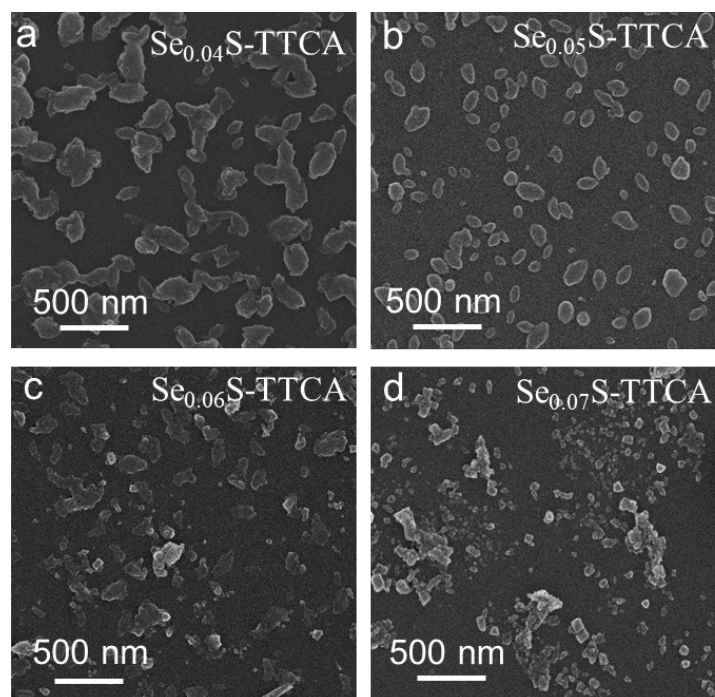
**Synthesis of  $\text{Se}_x\text{S}$ .** Se powder and S powder were evenly mixed in the mass ratio of 1:5, 1:10, 1:15 and 1:20. The mixture was ball milled at 200 rpm for 3 hours. It was then removed and sealed in a glass tube and heated in a muffle furnace at 260°C for 10 h at a rate of 5°C min<sup>-1</sup>. It was then removed and ground to obtain selenium sulfide ( $\text{Se}_x\text{S}$ ).

**Synthesis of  $\text{Se}_x\text{S}$ -TTCA.** The trithiocyanuric acid and the prepared  $\text{Se}_x\text{S}$  were homogeneously mixed in a mass ratio of 1:3 and heated at 160 °C in Ar atmosphere for 12 h, followed by heating at 245 °C for 3 h. The ring opening of the  $\text{Se}_x\text{S}$  and its reaction with the -SH of the TTCA was carried out by a second heating to form the Se-doped sulfur trithiocyanuric acid material ( $\text{Se}_x\text{S}$ -TTCA). The preparation of S-TTCA was identical to that of  $\text{Se}_x\text{S}$ -TTCA composites except that no selenium was added.

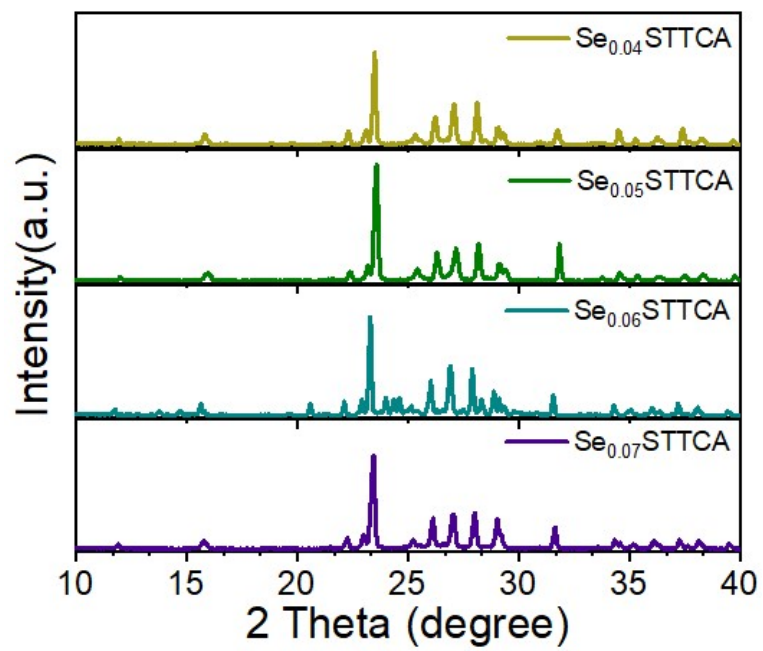
**Material characterizations.** The morphologies of the materials were recorded by using scanning electron microscope (SEM, Zeiss Supra55, accelerating voltage=20 kV). The crystalline structures of all the samples were identified by using Shimadzu XRD-6000 diffractometer (Cu K $\alpha$  source,  $\lambda = 1.5418 \text{ \AA}$ ). X-ray photoelectron spectroscopy (XPS) was carried out on Thermo Electron ESCALAB 250. Thermogravimetric analysis (TGA, HTIACHI STA7300) were used to test sulfur loadings. Fourier transform infrared spectroscopy (FTIR) spectra were analyzed on a Bruker Tensor II infrared spectrometer with KBr pellets. Raman spectra were recorded on a LabRAM Aramis Raman spectrometer (HORIBA Jobin Yvon). Organic elemental analyzer (GmbH vairo EL CUBE) was used to analyze the percentage of the elements.

**Li-S cell assembly and electrochemical characterizations.** The  $\text{Se}_x\text{S}$ -TTCA, super P and polyvinylidene fluoride (PVDF) were mixed with a mass ratio of 7:2:1 and put into N-methyl-2-pyrrolidone (NMP) solvent to prepare a slurry. The slurry was casted on the aluminum foil as a thin film and then vacuum dried at 60 °C for 12 h to serve as an electrode. The sulfur loading on each electrode was weighed to be  $\sim 2 \text{ mg cm}^{-2}$ , while was increased to  $4.1 \text{ mg cm}^{-2}$  for high-sulfur-loading cycling test. 2032 coin-type cells were assembled in the glove-box filled with Ar gas. Celgard 2400 PP separator was used as the separator and 1 M LiTFSI in DOL/DME (1:1 by volume) with 2.0 wt.%  $\text{LiNO}_3$  was used as the electrolyte. The electrolyte/sulfur ratio is estimated to be  $\sim 15 \mu\text{L mg}^{-1}$ . Galvanostatic discharge-charge tests were conducted on a Land battery test system (Land CT2001, Wuhan) at 25 °C in a potential range between 1.7 and 2.8 V. CV curves were collected in the potential range of 1.7–2.8 V at a scan rate of  $0.1 \text{ mV s}^{-1}$ . Electrochemical impedance spectra (EIS) were recorded with scan frequency from 100 kHz to 0.01 Hz at the open-circuit potential on a CHI 660E electrochemical workstation (Chenhua, Shanghai).

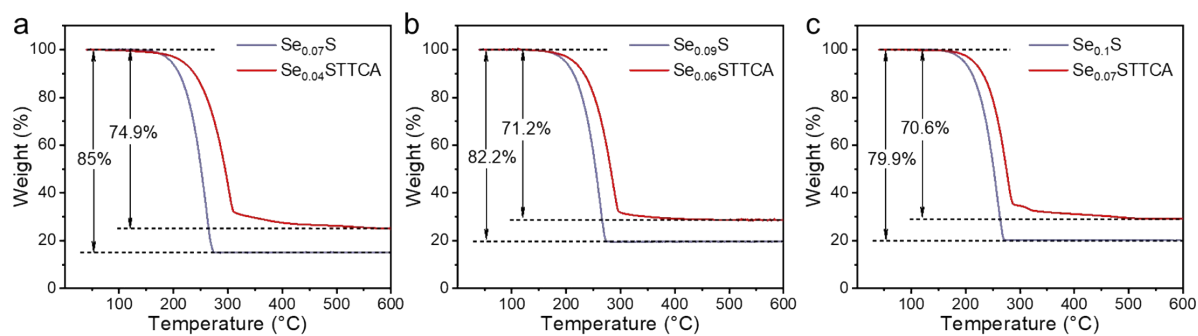
**Density-functional theory calculation.** All calculations were performed in the framework of the spin-polarized density functional theory (DFT) within the Projected Augmented Wave (PAW) method implemented in the Vienna ab initio simulation package (VASP). The revised Perdew-Burke-Ernzerhof (RPBE) function was adopted to describe electron exchange and correlation energy as it has been proven to provide a useful trend in calculating the adsorption energy. The cut-off energy for plane-wave basis was set as 400 eV to ensure the precision of calculations and the total energy convergence criterion for energy is  $10^{-5} \text{ eV}$ , with the force convergence thresholds set at  $0.02 \text{ eV}/\text{\AA}$  for geometric optimization.



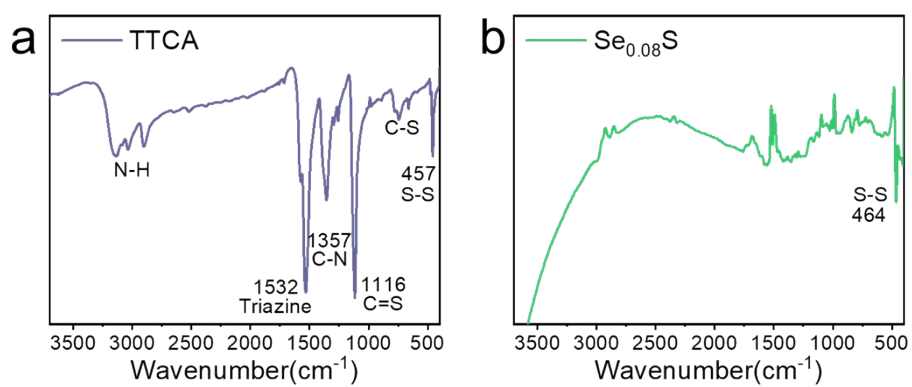
**Figure S1.** SEM image of  $\text{Se}_x\text{S-TTCA}$ .



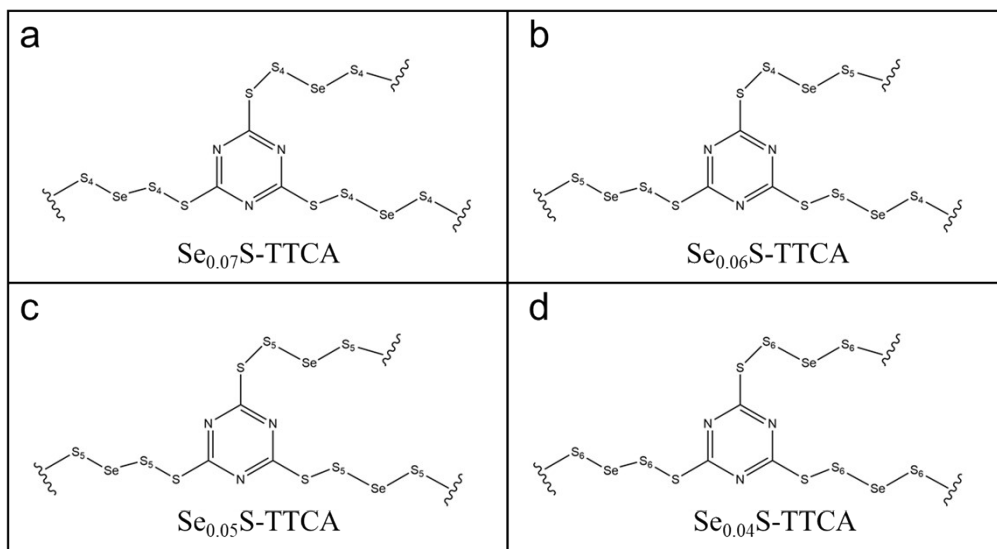
**Figure S2.** XRD pattern of  $\text{Se}_x\text{S-TTCA}$ .



**Figure S3.** TG curves of (a) Se<sub>0.07</sub>S and Se<sub>0.04</sub>S-TTCA, (b) Se<sub>0.09</sub>S and Se<sub>0.06</sub>S-TTCA, (c) Se<sub>0.1</sub>S and Se<sub>0.07</sub>S-TTCA.

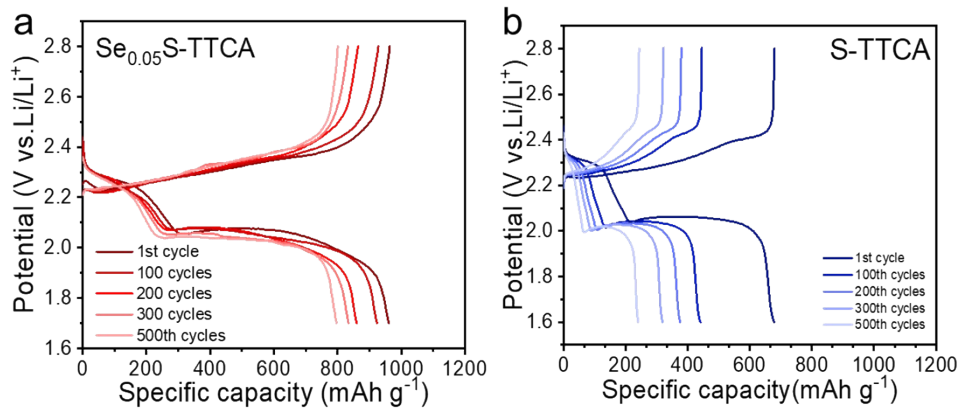


**Figure S4.** FTIR spectra of (a) TTCA and (b) Se<sub>0.08</sub>S.

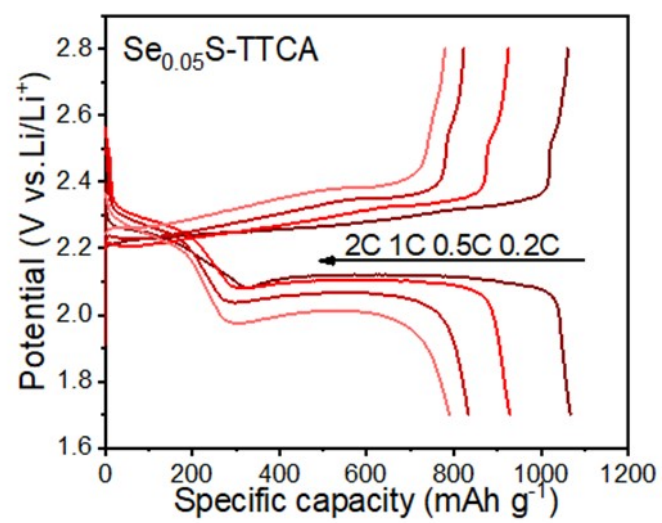


**Figure S5.** Chemical structure of (a)  $\text{Se}_{0.07}\text{S-TTCA}$ , (b)  $\text{Se}_{0.06}\text{S-TTCA}$ , (c)  $\text{Se}_{0.05}\text{S-TTCA}$ , and (d)  $\text{Se}_{0.04}\text{S-TTCA}$ .

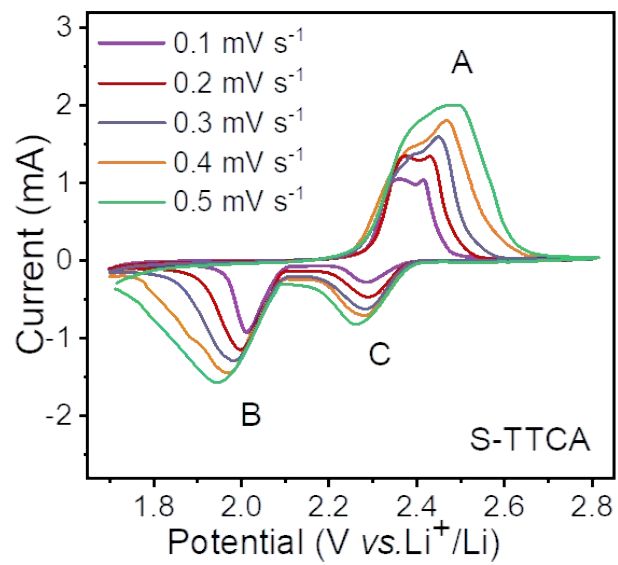




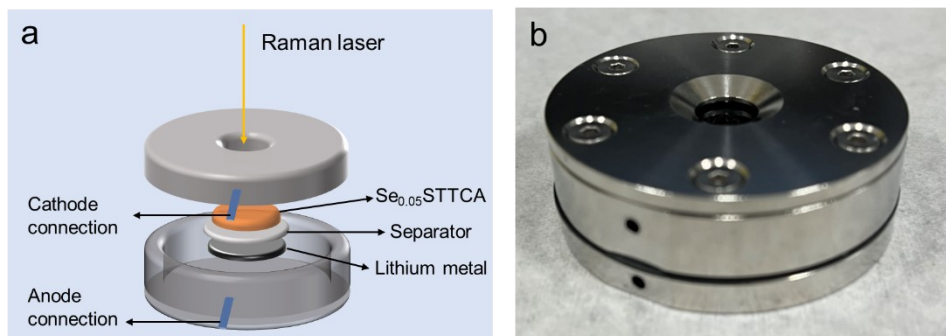
**Figure S6.** Charge/discharge profiles of (a) Se<sub>0.05</sub>S-TTCA and (b) S-TTCA electrodes.



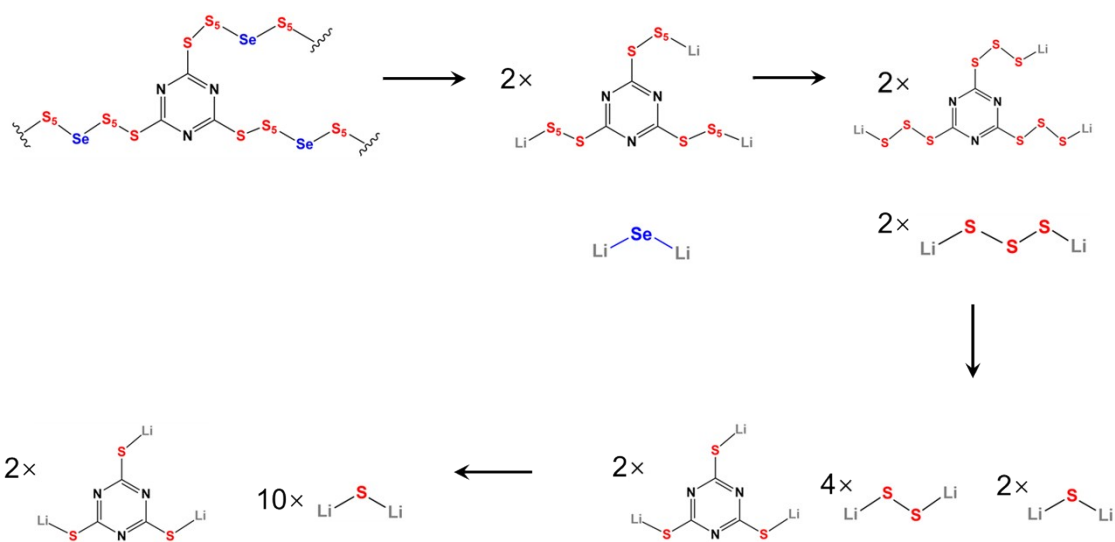
**Figure S7.** Charge/discharge profiles of  $\text{Se}_x\text{S-TTCA}$  electrode.



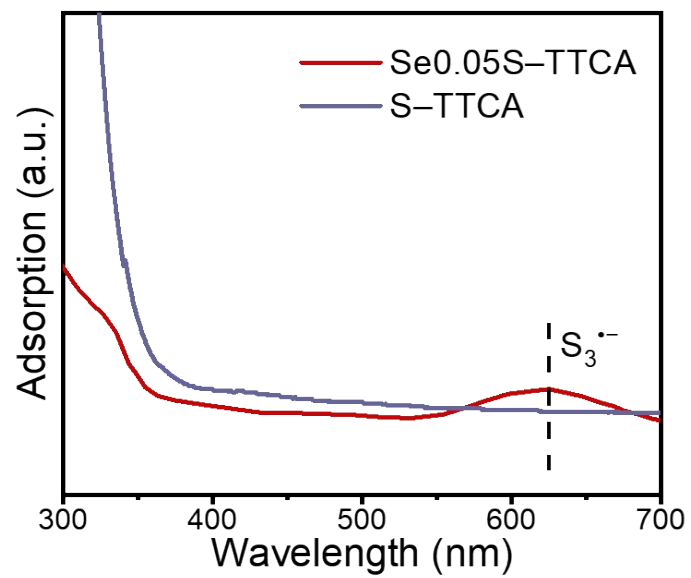
**Figure S8.** CV curves of S-TTCA electrode under different scanning rates from 0.1 to 0.5 mV s<sup>-1</sup>.



**Figure S9.** Test setup for in situ Raman spectroscopy.



**Figure S10.** The conversion mechanism of  $\text{Se}_{0.05}\text{S-TTCA}$ .



**Figure S11.** UV-Vis absorption spectra of the electrolyte in the Li||Se<sub>0.05</sub>S-TTCA cell and Li||S-C cell after discharging at 0.2 C.

**Table S1** Elemental analysis of selenium sulfide ( $\text{Se}_x\text{S}$ )

m (Se): m (S)	Material	S [%]	Se [%]	n (Se): n (S) after reaction
1:5	$\text{Se}_{0.1}\text{S}$	80.37	19.63	0.099
1:10	$\text{Se}_{0.09}\text{S}$	81.79	18.21	0.09
1:15	$\text{Se}_{0.08}\text{S}$	83.21	16.79	0.082
1:20	$\text{Se}_{0.07}\text{S}$	85.17	14.83	0.071

**Table S2** Elemental analysis of  $\text{Se}_x\text{S}$ -TTCA

Reactant	Material	N [%]	C [%]	H [%]	S [%]	Se [%]	n (Se): n (S) after reaction
$\text{Se}_{0.1}\text{S}+\text{TTCA}$	$\text{Se}_{0.07}\text{S}-\text{TTCA}$	9.48	8.27	0.03	70.5	11.72	0.07
$\text{Se}_{0.09}\text{S}+\text{TTCA}$	$\text{Se}_{0.06}\text{S}-\text{TTCA}$	10.12	8.6	0.02	71	10.26	0.06
$\text{Se}_{0.08}\text{S}+\text{TTCA}$	$\text{Se}_{0.05}\text{S}-\text{TTCA}$	9.84	8.42	0.03	72.3	9.41	0.05
$\text{Se}_{0.07}\text{S}+\text{TTCA}$	$\text{Se}_{0.04}\text{S}-\text{TTCA}$	9.16	7.96	0.04	74.78	8.06	0.04

**Table S3** Electrical conductivity results of S-TTCA and Se<sub>x</sub>S-TTCA

Materials	S-TTCA	Se <sub>0.04</sub> S-TTCA	Se <sub>0.05</sub> S-TTCA	Se <sub>0.06</sub> S-TTCA	Se <sub>0.07</sub> S-TTCA
Electrical conductivity 10 <sup>-8</sup> S cm <sup>-1</sup>	5.06	8.44	8.76	9.05	9.33

**Table S4** Compacted densities of S-TTCA and Se<sub>x</sub>S-TTCA

	S-TTCA	Se <sub>0.04</sub> S-TTCA	Se <sub>0.05</sub> S-TTCA	Se <sub>0.06</sub> S-TTCA	Se <sub>0.07</sub> S-TTCA
20KN tableting thickness (mm)	4.084	3.716	3.684	3.653	3.598
20KN tableting density (g cm <sup>-3</sup> )	1.845	2.027	2.045	2.062	2.094



**Table S5** Compacted densities of Se<sub>0.05</sub>S-TTCA cathodes and other counterparts

	Super P	AC	CNF	GO	CNT	SeS <sub>0.05</sub> -TTCA
20KN tableting thickness (mm)	5.851	5.773	5.453	4.419	3.877	3.684
20KN tableting density (g cm <sup>-3</sup> )	1.288	1.305	1.382	1.705	1.943	2.045

**Table S6** Theoretical specific capacity of Se<sub>x</sub>S-TTCA

Material	S [%]	Se[%]	Specific capacity of Se (mAh g <sup>-1</sup> )	Specific capacity of S (mAh g <sup>-1</sup> )	Theoretical specific capacity (mAh g <sup>-1</sup> )
Se <sub>0.07</sub> STTCA	70.5	11.72	96.6	1436.2	1532.8
Se <sub>0.06</sub> STTCA	71	10.26	85.6	1463.5	1549.1
Se <sub>0.05</sub> STTCA	72.3	9.41	78.0	1482.1	1560.1
Se <sub>0.04</sub> STTCA	74.78	8.06	66.0	1513.9	1579.9