

## Supporting Information:

### **One-pot synthesis of nitrogen-doped carbons with hierarchically micro- and mesoporous structure for supercapacitor and CO<sub>2</sub> capture**

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## **1. Experimental Section**

### **1.1 Preparation of TUD based “molecular basket” solid amine sorbents**

The solid amine sorbents were prepared through wet impregnation method which has been reported in our previous studies [S1, S2]. The solid sorbent was named xA/TUD-y while x, A and y represent the amine loading, TEPA and the carbonization temperature, respectively. For example, 50A/TUD-700 means that the carbon which is obtained through carbonization at 700°C was used as amine support, and the nominal TEPA loading is 50%. Since the carbons have high surface areas, nanometer-thick films were formed on the surfaces of carbons.

### **1.2 Characterization methods**

The morphologies of the samples were analyzed on a scanning electron microscopy (Hitachi S-4800) and a transmission electronic microscopy (JEM-2100F). N<sub>2</sub> adsorption-desorption isotherms were characterized by Quantachrome Autosorb-1 surface and pore size analyzer under liquid nitrogen temperature (-196°C). The samples were degassed at 200°C for at least 4 h. The surface area was calculated using the multipoint Brunauer-Emmett-Teller (BET) method. The total pore volume ( $V_t$ ) was determined as the volume of liquid nitrogen adsorbed at a relative pressure of 0.99. X-Ray Photoelectron Spectroscopy (XPS) analysis was measured on an ESCALAB 250XI spectrometer (Thermo). Raman spectra were measured on a Renishaw inVia RM10000 spectrograph with an excitation wavelength of 532 nm. Elemental analysis was measured on Vario EL III elemental analyzer (Elementar).

### 1.3 The Electrochemical measurements and the calculation method of specific capacitance.

All electrochemical measurements were carried out on a Chenhua CHI660E electrochemical workstation. The electrochemical performances of electrode materials were measured through cyclic voltammetry (CV), galvanotatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS). In a three-electrode system, Pt served as counter electrode, Hg/HgO served as reference electrode and N-doped carbon materials served as the working electrode. The prepared Carbon material, polytetrafluoroethylene and acetylene carbon black with ratio of 90:5:5 were mixed and then daubed on 1×2 cm nickel foam and flatten under 10 MPa. The mass of electrode material on the nickel foam was ~2 mg.

The specific capacitances ( $C$ , F g<sup>-1</sup>) of electrode materials were calculated based on the galvanotatic charge-discharge curve according to the formula

$$C = \frac{I}{m} \times \frac{\Delta t}{\Delta V} \quad (\text{S1})$$

here,  $I$  is discharge current (A),  $\Delta t$  is discharge time (s),  $\Delta V$  is voltage change excluding voltage drop (IR drop) during the process of discharging,  $m$  is the mass of active electrode material (g).

In a two-electrode system (Fig.s S1 and S2), two pieces of nickel foams coated with equal carbon materials were separated by Celgard@3501 membrane and assembled into a home-made symmetrical Swagelok cell (Fig. S1). The specific capacitances ( $C_s$ , F g<sup>-1</sup>) were calculated based on the galvanotatic charge-discharge curve according to the following formula

$$C_s = 4 \times C_{cell} = 4 \times \frac{I}{m_{total}} \times \frac{\Delta t}{\Delta V} = 2 \times \frac{I}{m_s} \times \frac{\Delta t}{\Delta V} \quad (S2)$$

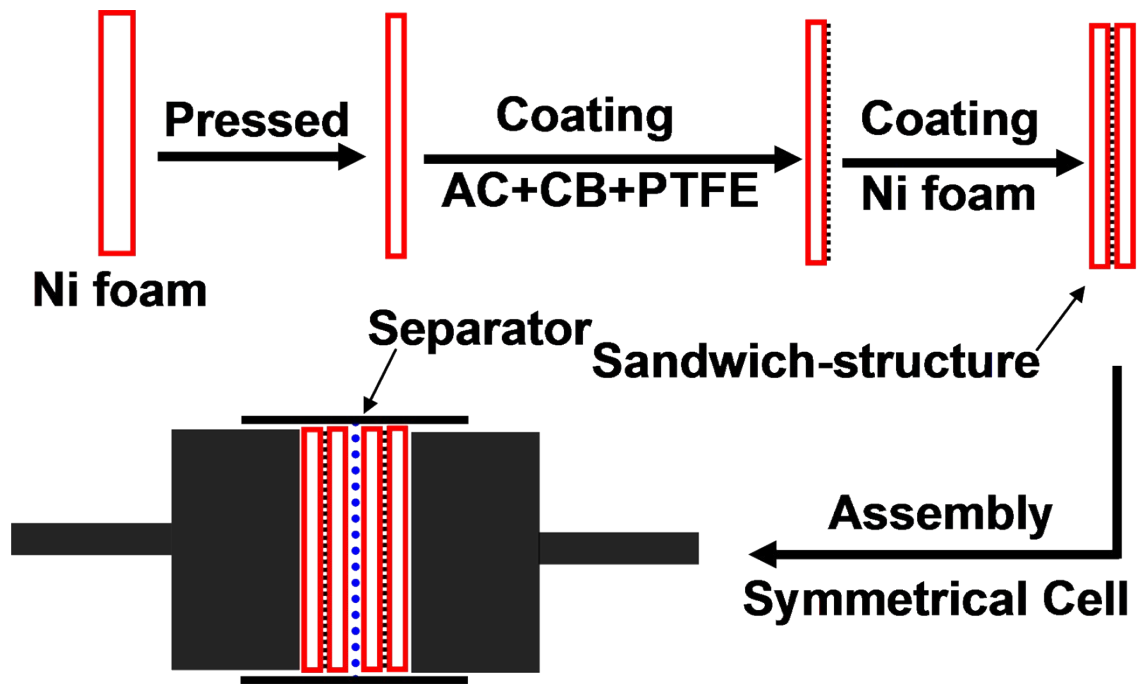
here,  $C_s$ ,  $C_{cell}$ ,  $m_{total}$ ,  $m_s$ ,  $I$ ,  $\Delta t$  and  $\Delta V$  are the specific capacitance of a single electrode ( $F g^{-1}$ ), the specific capacitance of the Swagelok cell ( $F g^{-1}$ ), the total mass of active electrode material in two electrodes (g), the mass of active electrode material in single electrode (g), the discharge current (A), the discharge time (s) and the voltage change excluding voltage drop (IR drop) during the discharging process, respectively. In this study, we used the mass of active electrode material in single electrode (g) to set the charge-discharge current and used the latter formula to calculate  $C_s$ . The energy density and power density of supercapacitors were calculated according to the following formula

$$E = \frac{1}{2} \times \frac{C_{cell} \Delta V^2}{3.6} = \frac{\Delta V^2}{7.2} \times \frac{I}{m_{total}} \times \frac{\Delta t}{\Delta V} \quad (S3)$$

$$P = \frac{3600E}{\Delta t} \quad (S4)$$

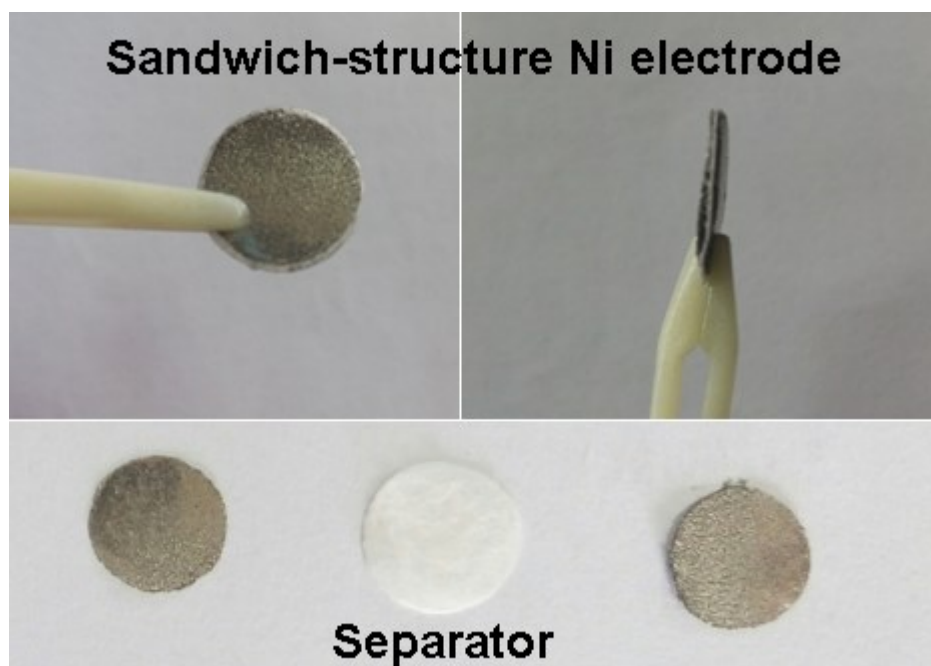
$E$  is the energy density ( $Wh Kg^{-1}$ ),  $P$  is the power density ( $W Kg^{-1}$ ),  $V$  is virtual voltage change (V) and  $t$  is the discharging time (s), respectively [S3-S7].

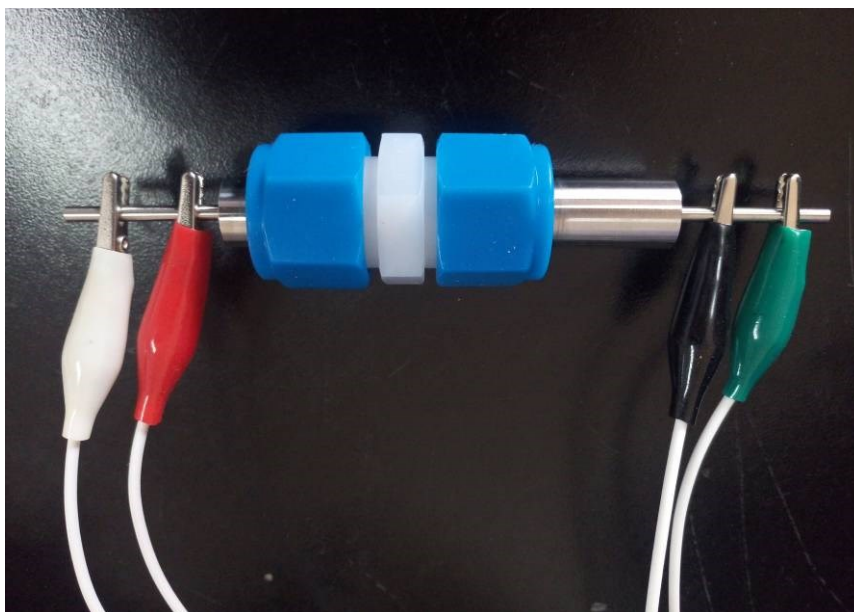
The electrochemical impedance spectroscopy of electrode materials was tested in a frequency range from 0.005 Hz to 100 KHz.



**AC:** activated carbon  
**CB:** acetylene carbon black  
**PTFE:** polytetrafluoroethylene

**Fig. S1** The preparation of Electrodes in two-electrode system.





**Fig. S2** The home-made swagelok-type cell used in two-electrode system.

#### **1.4 CO<sub>2</sub> sorption performance test**

The static adsorption of CO<sub>2</sub> on carbons were performed by Quantachrome Autosorb-1 surface and pore size analyzer under 0 and 25°C.

The dynamic CO<sub>2</sub> sorption on carbons and carbon based “molecular basket” sorbents were conducted by a fixed-bed reactor system as shown in Fig. S3. The sorption process was operated at atmospheric pressure and the outlet gases were analyzed by an online Mass Spectrometry (MS, OminiStar 200). In the reactor, 0.30 g of dried sorbent was packed into the middle of the quartz-tube reactor (6 mm inner diameter) heated by heating tape. In our previous studies [S8], it was found that 75°C is the optimal temperature for CO<sub>2</sub> capture performance which may be due to the stronger interaction between CO<sub>2</sub> and amine at elevated temperature. Therefore, 75°C

also was chosen as the adsorption temperature in the current study. Prior to each adsorption measurement, the sorbent was firstly activated by heating to 100°C and kept for 1 h in He stream at a flow rate of 20 mL/min. After cooling to the 75°C, 10% CO<sub>2</sub> balanced with N<sub>2</sub> stream at a total flow rate of 10 mL/min was introduced and passed through the adsorbent bed until adsorbent saturation was reached.

For pure TEPA, 0.3 g liquid TEPA was placed into the middle of the quartz-tube reactor to test its CO<sub>2</sub> sorption performance.

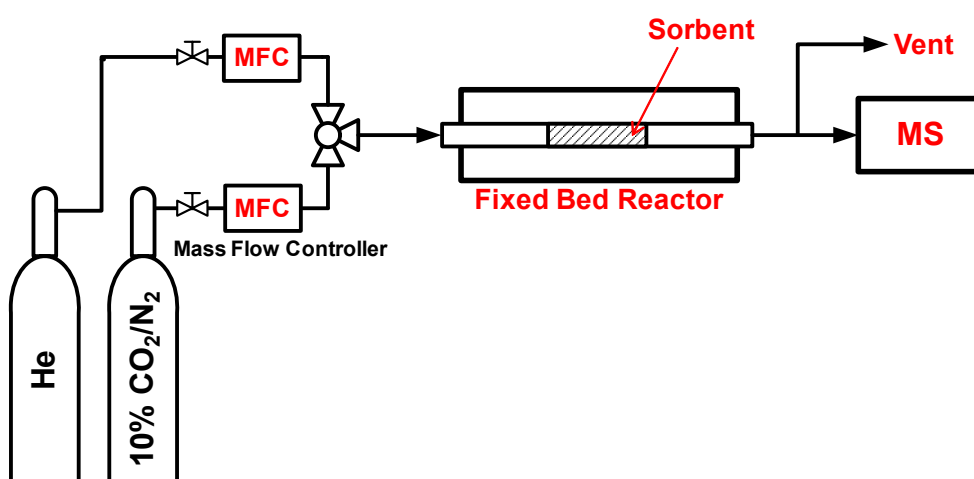


Fig. S3 Schematic diagram of the fixed-bed reactor system.

## 2. Additional results

**Table S1.** The elemental contents and the surface species contents.

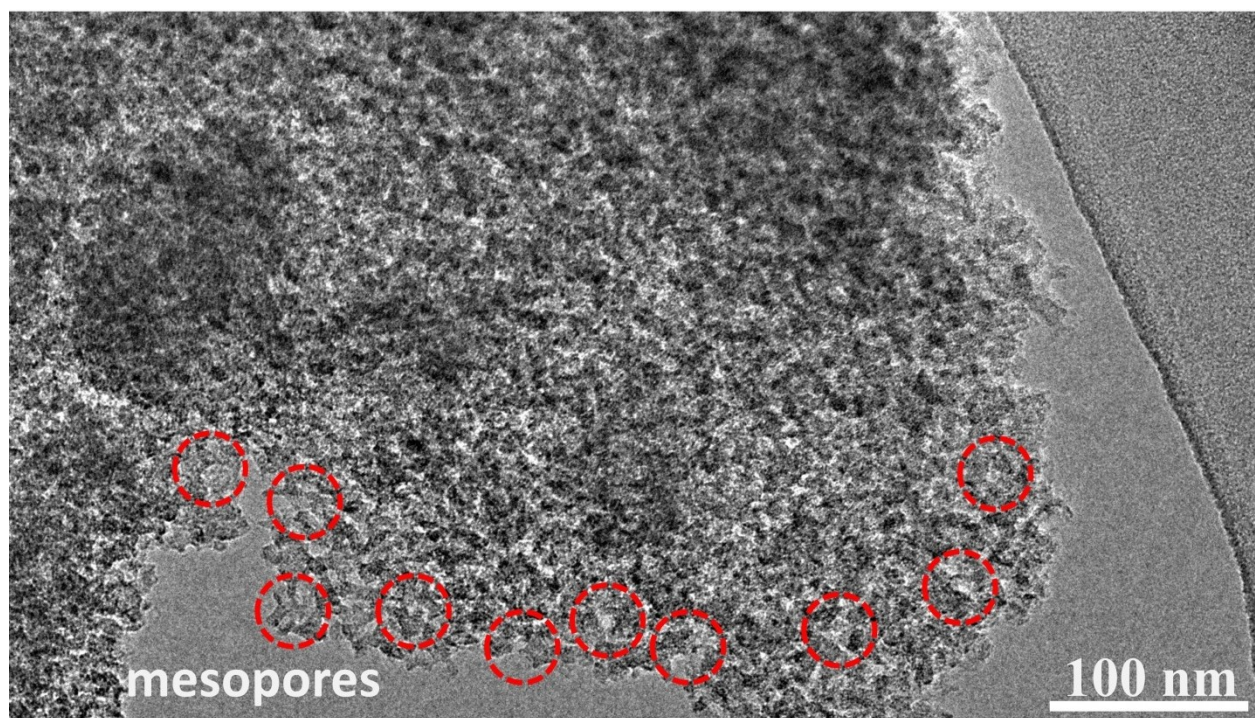
Samples	C <sup>a</sup> (%)	H <sup>a</sup> (%)	O <sup>a</sup> (%)	N <sup>a</sup> (%)
TUD-600	85.68	1.25	4.80	8.27
TUD-700	87.39	1.12	4.13	7.36
TUD-800	89.51	1.01	3.36	6.12
TUD-900	90.61	0.92	2.82	5.65

<sup>a</sup>The elemental contents were measured using elemental analyzer.



**Fig. S4.** The Enlarged images of mixture solution and the formed foam for clear view.





**Fig. S5** Enlarged TEM images of TUD-700 for clear view.

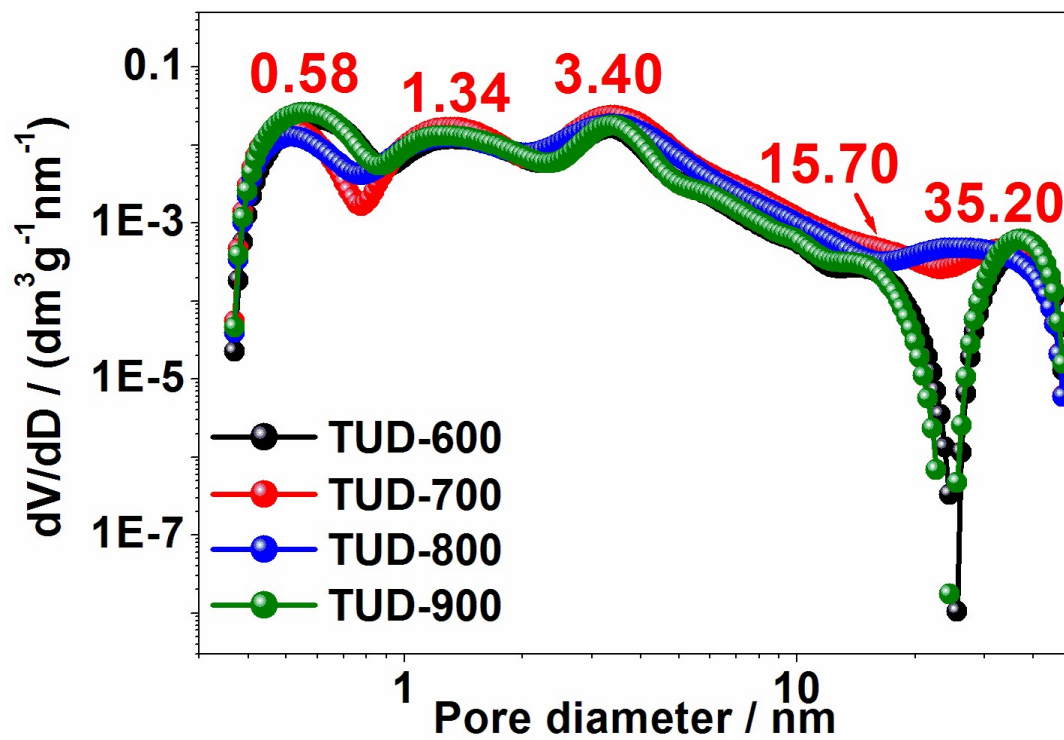


Fig. S6 Pore size distributions of TUD-600, TUD-700, TUD-800 and TUD-900 in log format.

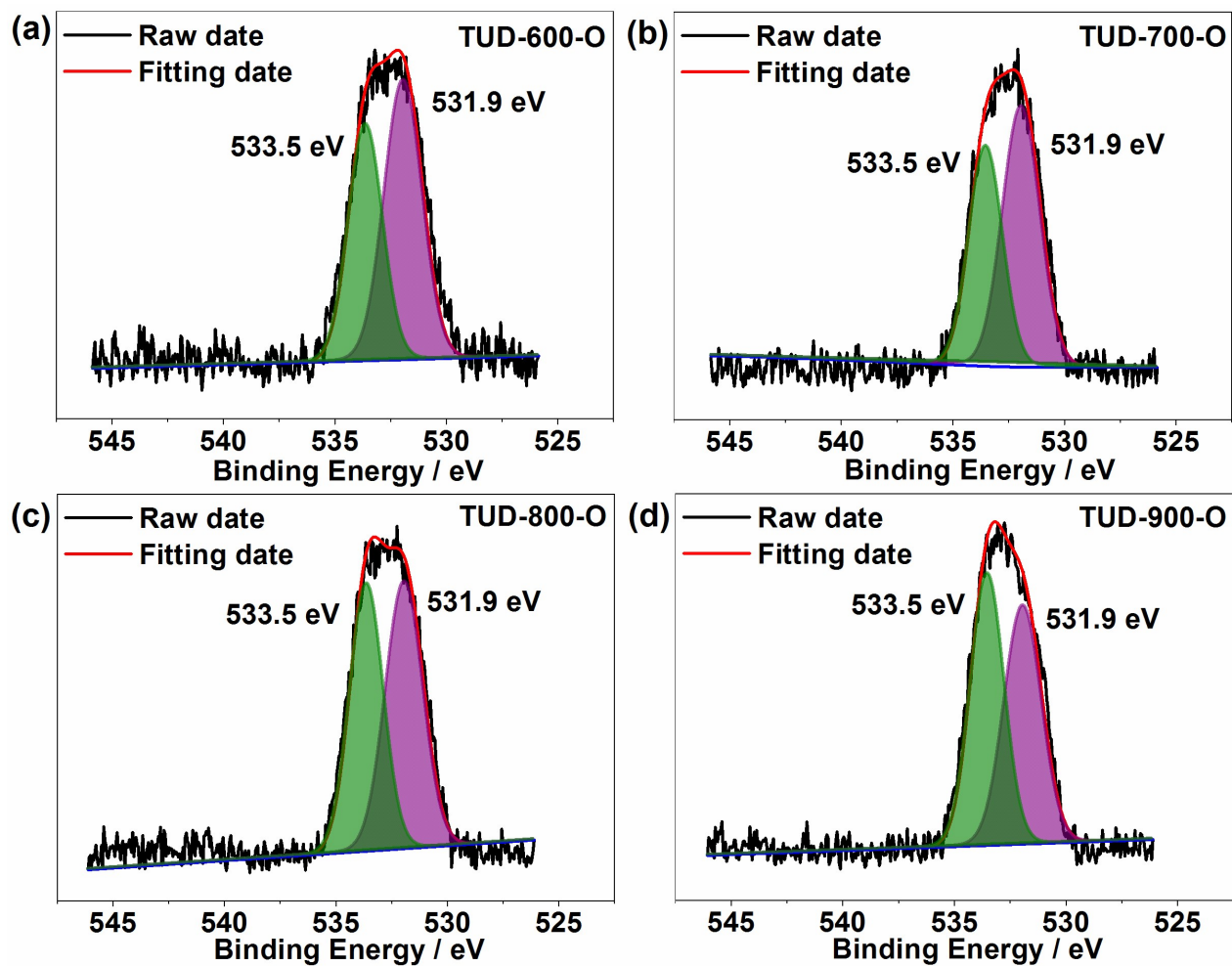
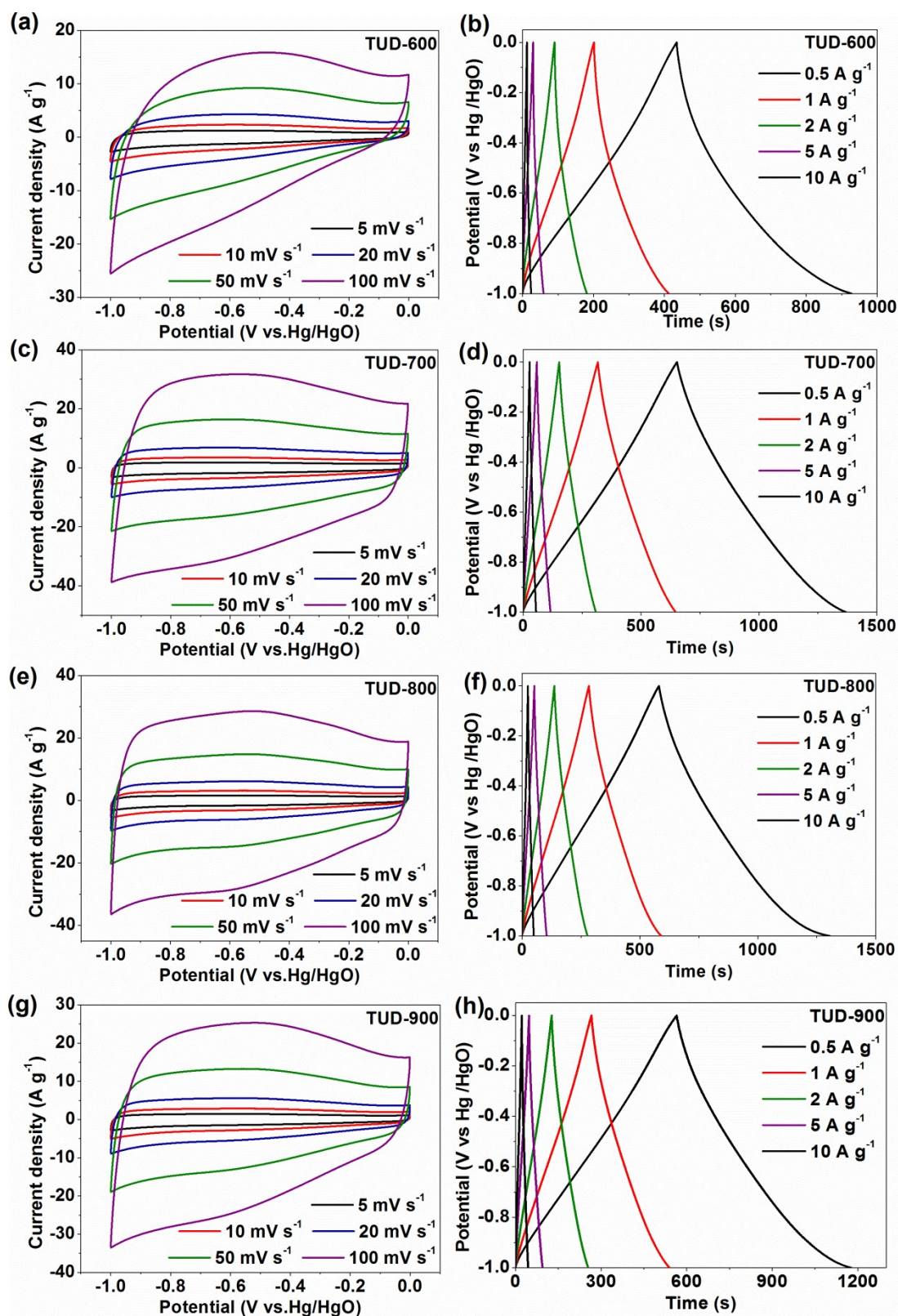


Fig. S7 O1s spectra of TUD-600, TUD-700, TUD-800 and TUD-900.



**Fig. S8** The electrochemical performances of TUD-600, TUD-700, TUD-800 and TUD-900 in three-electrode system in KOH electrolyte. (a)(c)(e)(g) CV curves at different scanning rates; (b)(d)(f)(h) GCD curves at different current densities.

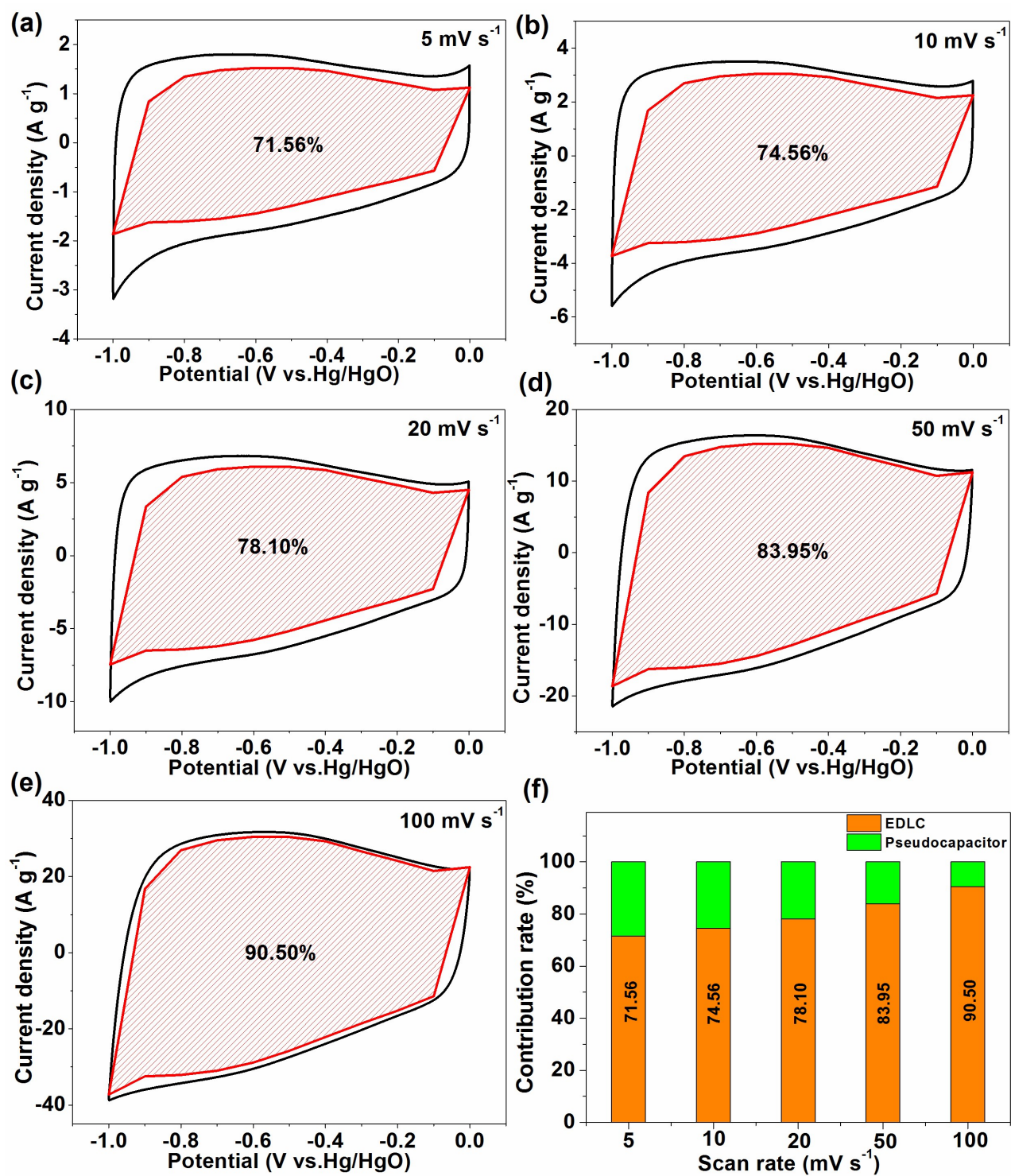
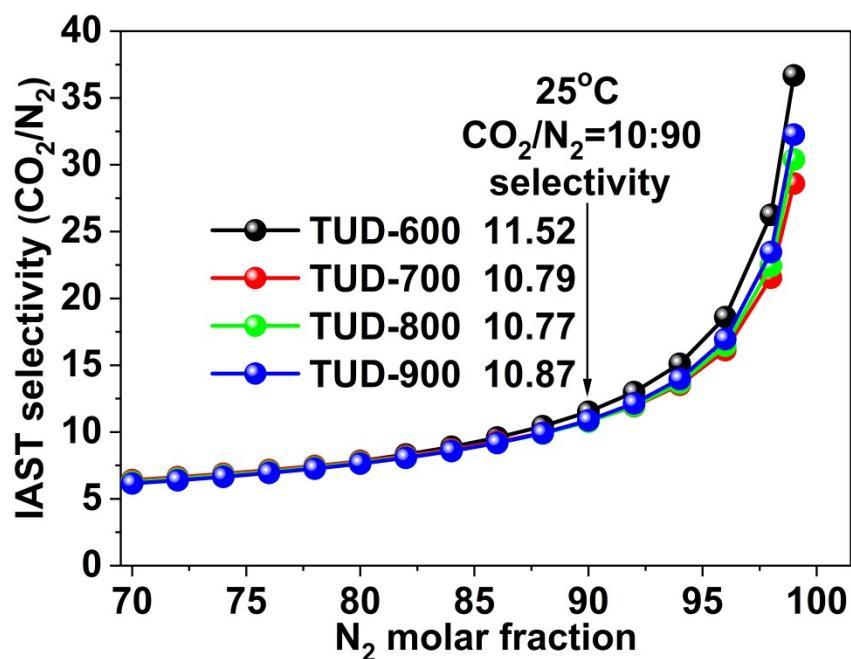


Fig. S9 The contributions of the electric double-layer capacitance (EDLC) and the pseudocapacitance for TUD-700.



**Fig. S10** TUD-600, TUD-700, TUD-800 and TUD-900 selectivity at 25°C.

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