Supporting Information

Influence of halogen elements in organic salts on n-type doping of CNT yarn for thermoelectric applications

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KEYWORDS

CNT, halide, thermoelectric, thermal conductivity, electrical conductivity, Seebeck coefficient, yarn

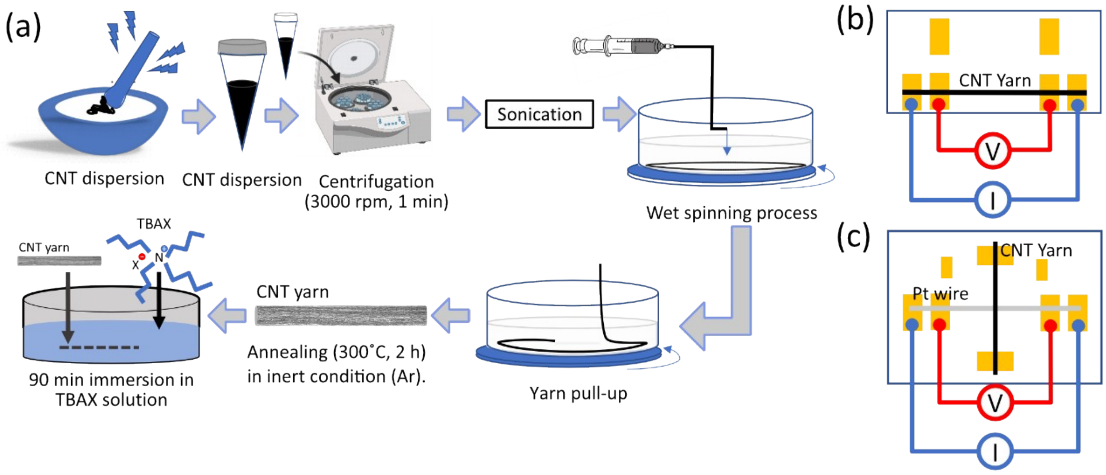

Fig. S1 (a) Fabrication and doping processes for CNT yarn. (b) and (c) Schematic plan view of the electrode-substrate used for Seebeck coefficient and *I-V* measurements, and the DC heating cross-junction method for thermal conductivity measurements, respectively.

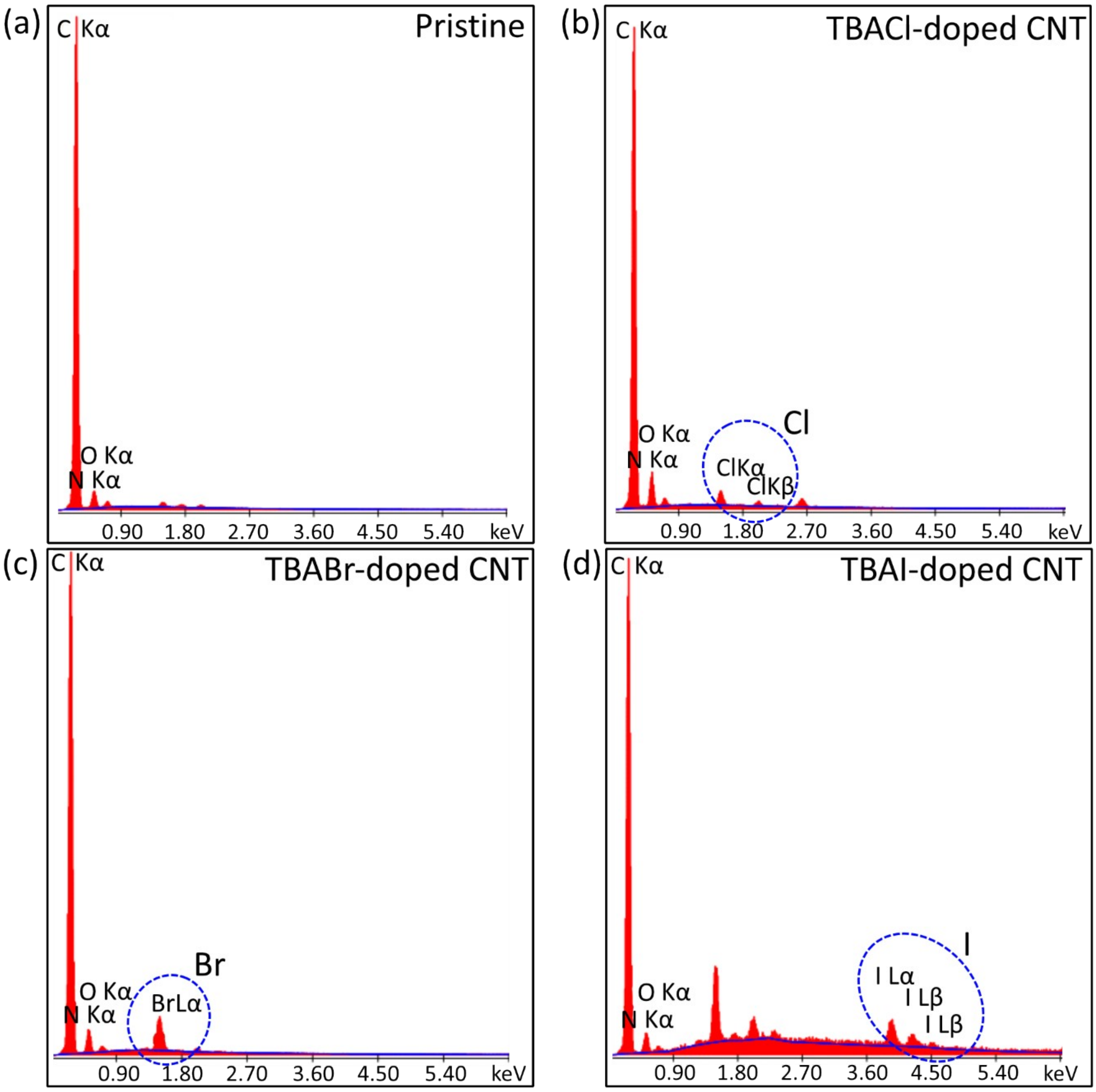

Fig. S2 EDX spectra of TBAX-doped CNT yarn.

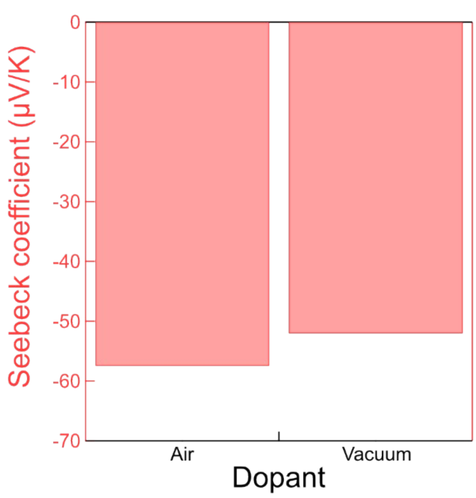

Fig. S3 Comparison of the Seebeck coefficients measured under ambient and vacuum conditions.

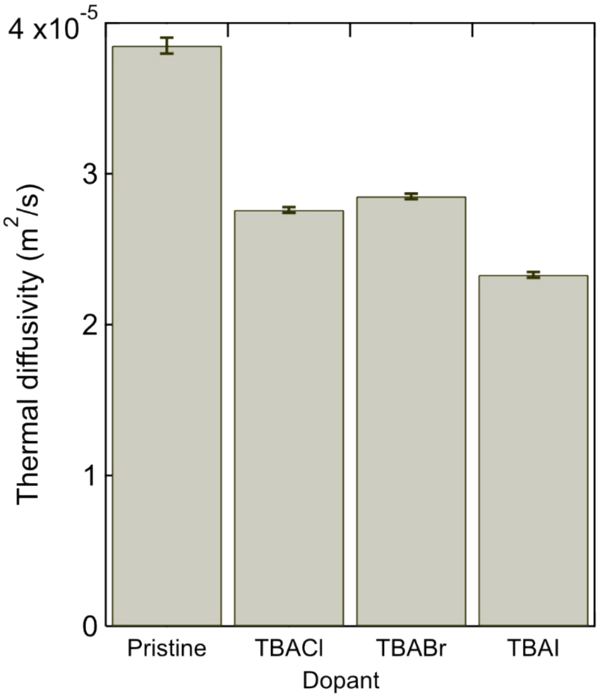

Fig. S4 Thermal diffusivity of TBAX-doped yarns.

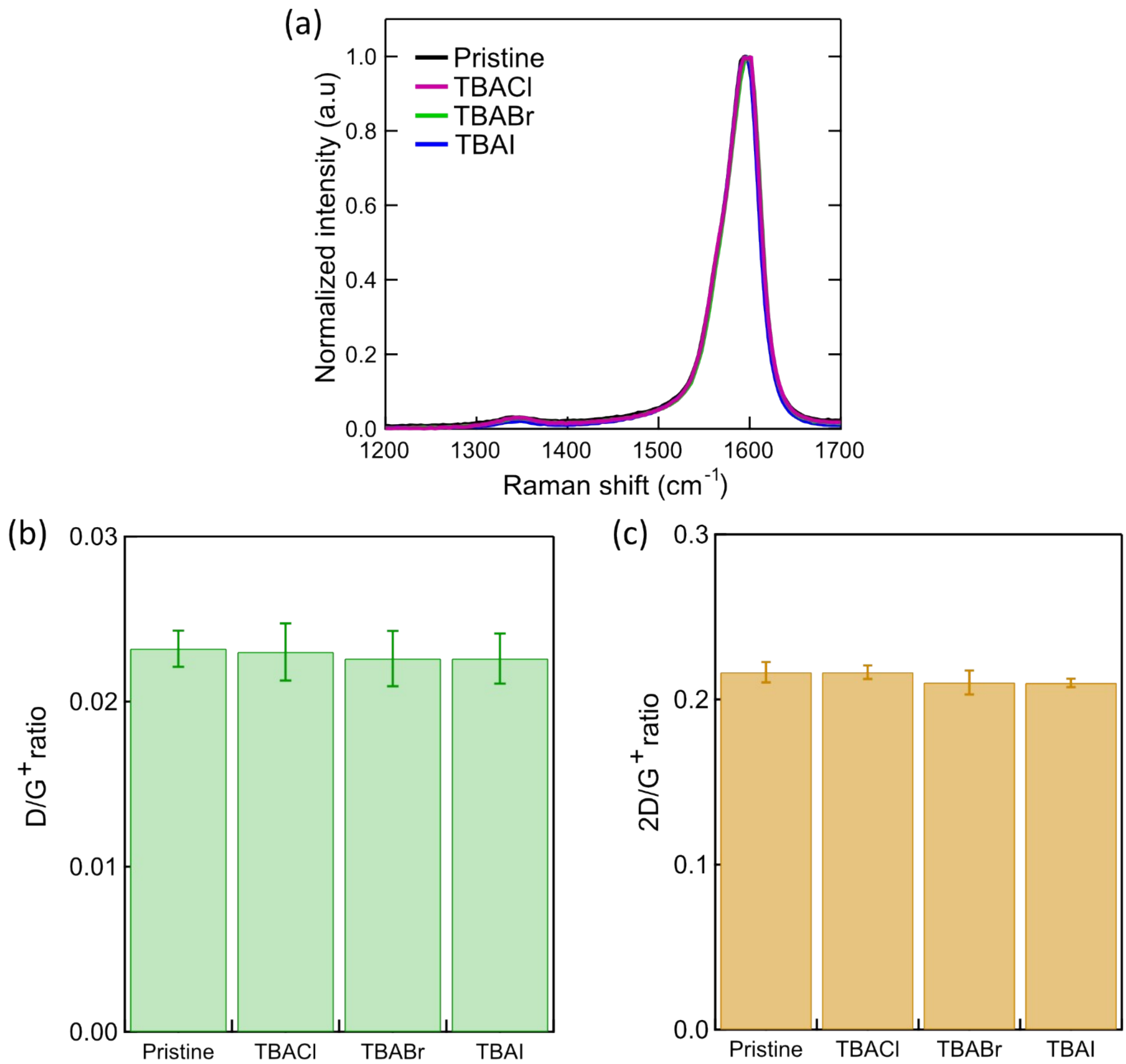

Fig. S5 (a) Comparison of the Raman G^+-band spectra. (b) D/G^+ and (c) $2D/G^+$ ratios of pristine and TBAX-doped CNT yarns.

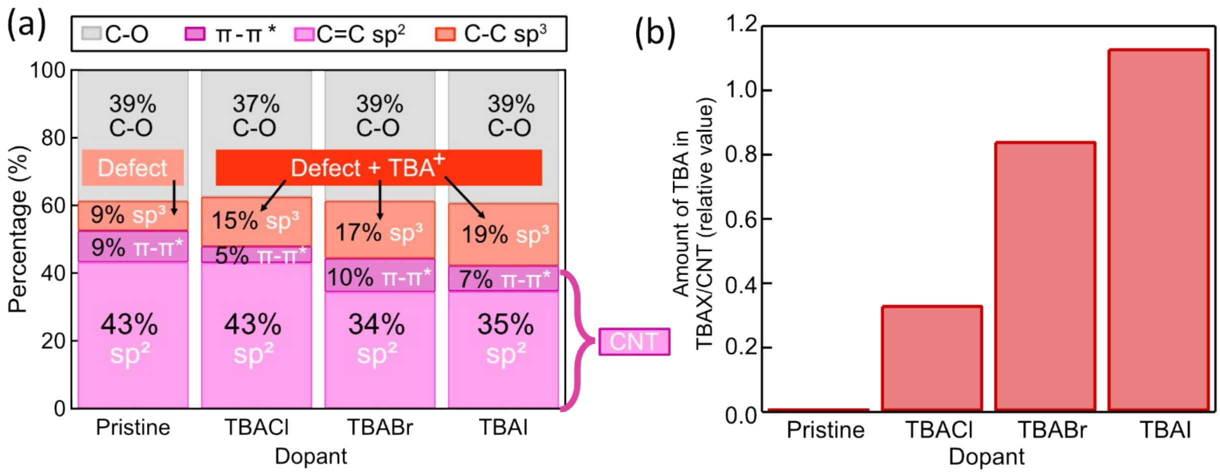

Fig. S6 (a) Chemical compositions calculated from the XPS C1s spectra of pristine and TBAX-doped yarns. (b) Relative amount of TBA in the CNT yarns.

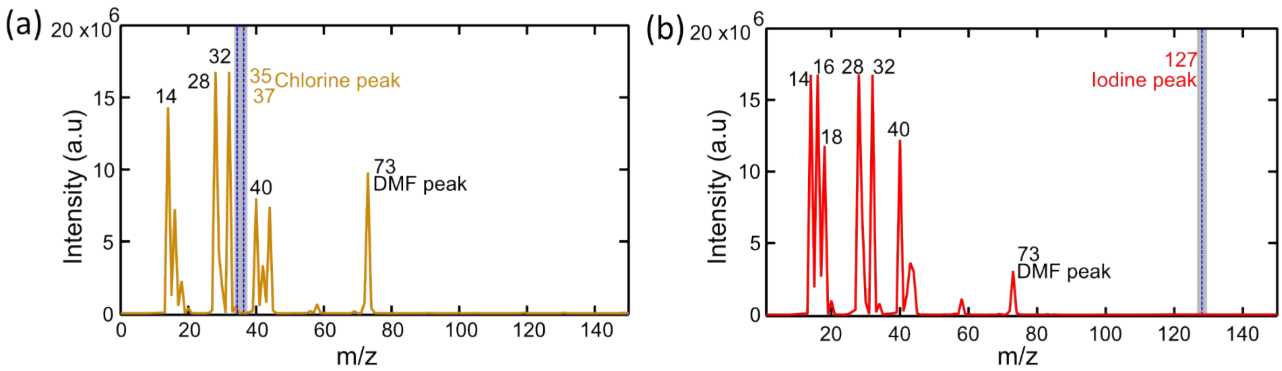

Fig. S7 Gas-phase mass spectra measured during (a) TBACl and (b) TBAI doping treatment. The chemical ionization was used and negative ions are detected. The dashed lines indicate the expected position of the chlorine and iodine peaks, respectively. All of the visible peaks can be assigned to the mother and daughter ions of DMF.

Estimation of the amount of halogen molecules generated during the doping treatment

1. **Maximum amount of generated X_2 from a small tube**

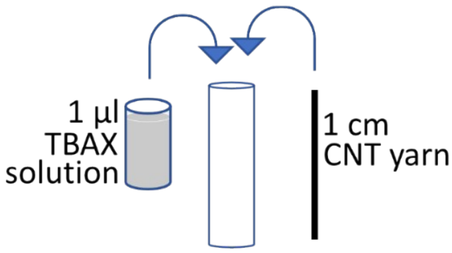

Fig. S8 Preparation for mass spectroscopy measurement.

CNT length	1 cm
CNT volume	6.3×10^{-5} cm^3
CNT density	0.79 g cm^{-3}
CNT Molecular weight	12 g mol^{-1}
DMF molecular weight	73.1 g mol^{-1}
Density of DMF	0.95 g ml^{-1}

- Total amount of DMF in the test tube

1 µl DMF → 0.95 g ml^{-1} × 1 µl = 9.5×10^{-4} g

$$\frac{9.5 \times 10^{-4}\, g}{73.1\, g\, mol^{-1}} = 1.3 \times 10^{-5}\, mol = 13\, \mu mol$$

- Total amount of X^- in the test tube

1 µl TBAX solution → Concentration TBAX 0.54 M = 0.54 mol l^{-1}= 0.54 µmol

Ratio of TBA^+ and X^- based on TBAX formula is 1:1

Maximum amount of X^- in 1 µl of TBAX solution → 0.54 µmol.

This is only ca. 4% of the amount of DMF.

2. **Estimated amount of DMF vapor**

Here, we try to roughly estimate the amount of DMF molecules injected into the mass spectrometer. First, we assume that the space in the small test tube (0.044 cm^3) is filled with the DMF molecules with saturated vapor pressure just before injection. From the vapor pressure of DMF at 20°C (3.6×10^2 Pa), the amount of the DMF vapor is calculated to be 4.16 µmol. This must be an approximate amount of DMF molecules possibly injected into the mass spectrometer. From the previous calculation we know that amount of halogen is about 4% from amount of DMF. Therefore, the approximate maximum amount of halogen vapor is around 0.17 µmol.

3. Estimated X_2 generation from XPS results

- Amount of carbon in 1 cm CNT

$0.79\ g\ cm^{-3} \times 6.3 \times 10^{-5}\ cm^3 = 4.977 \times 10^{-5}\ g$

$$\frac{4.977 \times 10^{-5}\,g}{12\,g\,mol^{-1}} = 0.41 \times 10^{-5}\,mol = 4.1\,\mu mol$$

- Ratio of X/C (halogen) from XPS results with maximum value is 0.0089

maximum amount of X^- in 1 cm CNT → 0.0089 × 4.1 μmol = 0.0365 μmol = 36.5 nmol

- Ratio of N/C from XPS results (maximum value) is 0.0259

maximum amount of TBA^+ in 1 cm CNT → 0.0259 × 4.1 μmol = 0.1062 μmol = 106.2 nmol

- The amount of X_2 generation in a 1 cm CNT is calculated by subtraction of N/C and X/C

106.2 nmol - 36.5 nmol = 69.7 nmol

Therefore, the amount of halogen is considered to be much smaller than the amount of DMF.

4. Estimated X_2 generation from charge carrier amount

Considering the electrical conductivity (around 1000 S/cm) and hole mobility of SWCNT (10^2~10^5 cm^2/Vs), the carrier concentration of CNT yarn would be in the order of 10^{16}~10^{19}/cm^3.[1234] Volume of CNT yarn that we used is 6.3×10^{-5} cm^3. Then, the number of carriers in 1 cm of CNT yarn is around 6.3×10^{11}~10^{14}. After that, we try to calculate the halogen amount generated by the transfer to the CNT yarn and it is around $1.05 \times 10^{-9} \sim 10^{-12}$ mol = 10^0~10^{-3} nmol.

Therefore, the amount of halogen is again considered to be much smaller than the amount of DMF.

Regarding the concentration of 0.54 M TBAX, it is estimated to be around 3.3×10^{20} molecules/cm^3, higher than the carrier concentration of CNT that might be dense enough to hide the change by doping process. This calculation and unreacted TBAX molecules also support that halogen generation cannot be easily detected regardless analysis method due to the weak doping level.

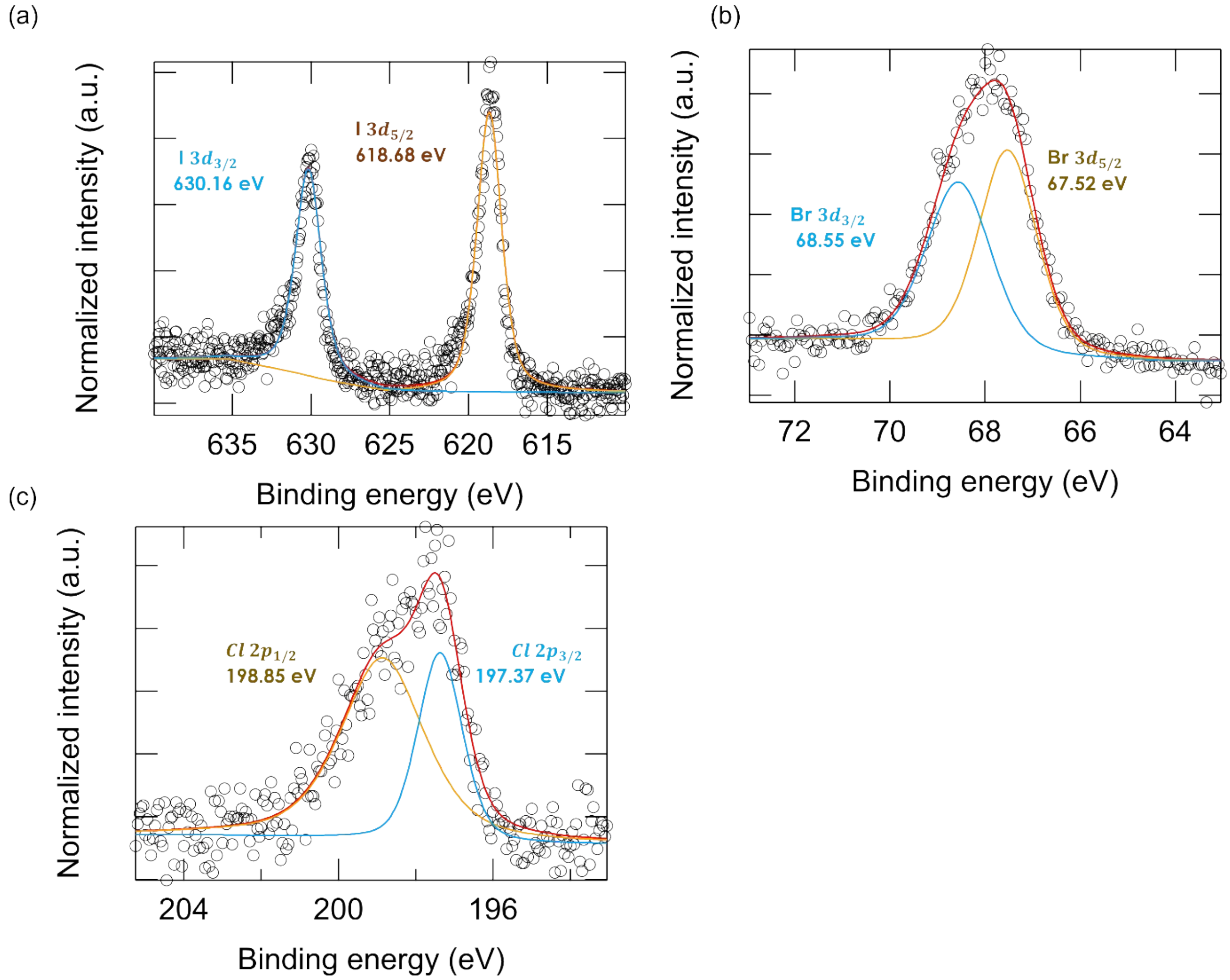

Fig. S9 XPS spectra of TBAX-doped CNT yarns: (a) I3d peaks from TBAI-doped, (b). Br3d peaks from TBABr-doped, and (c) Cl2p peaks from TBACl-doped CNT yarns. All of these spectra are well-fitted by the single component of halogen atoms without any shoulder peaks.

Reference

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