2nd Joint Workshop on
Measurement Issues in CNTs

Raman spectroscopy and TGA of sonicated SWCNTs with artificial defects

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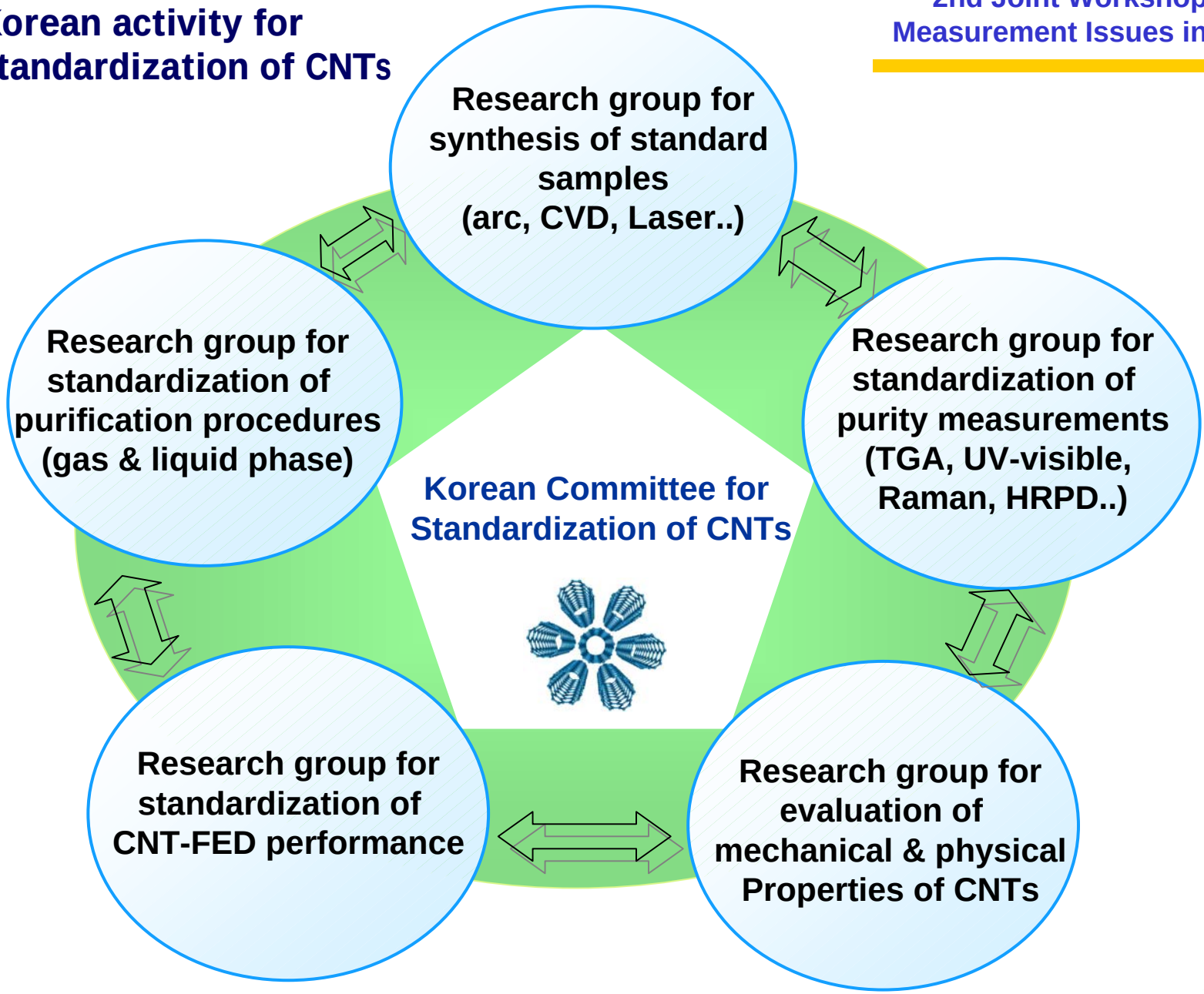
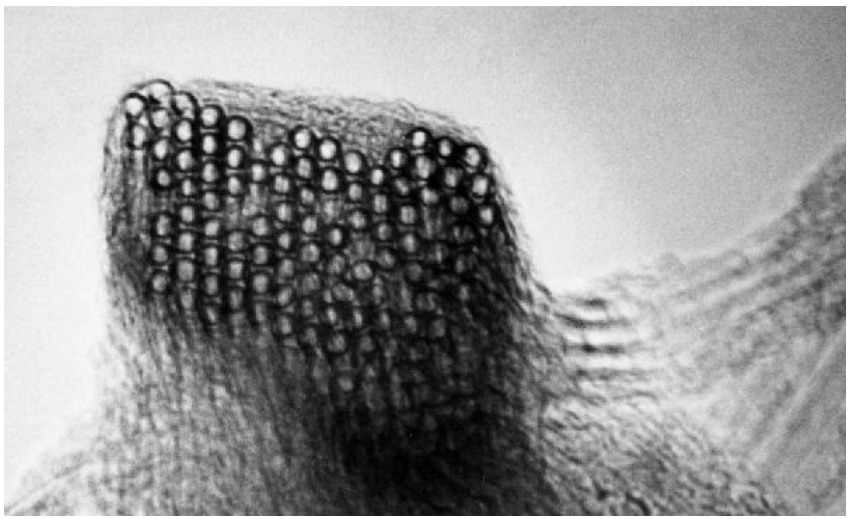
Korean activity for standardization of CNTs

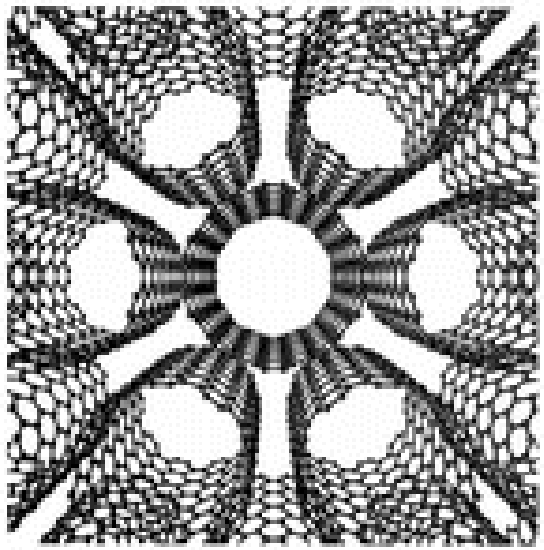


What is a bottleneck in CNT application?

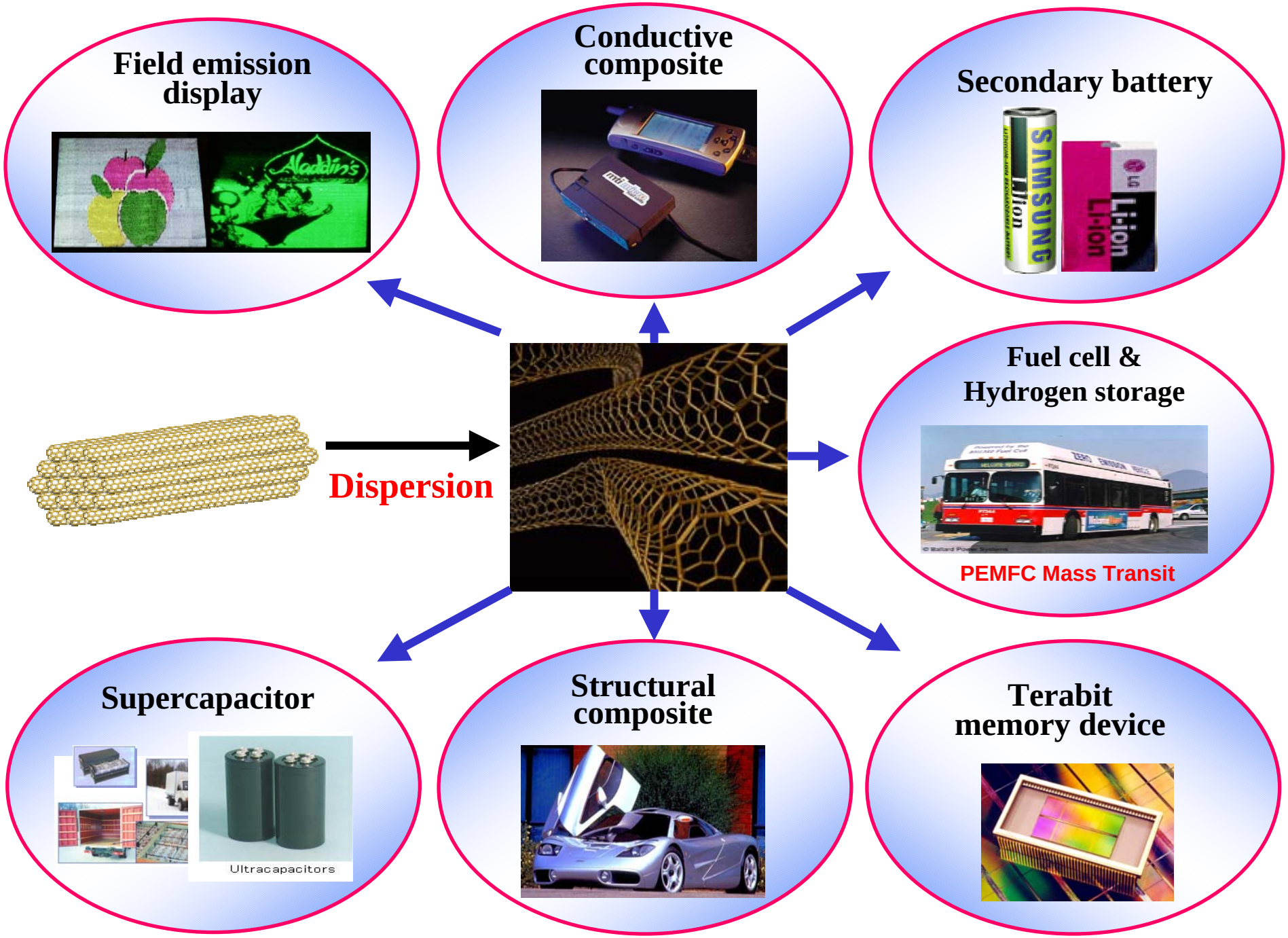
- **Ropes: bundles of SWCNTs**
  - **triangular array of individual SWCNTs**
  - **ten to several hundreds tubes**
  - **typically in a rope, tubes of different diameters and chiralities**



(From R. Smalley´s web image gallery)

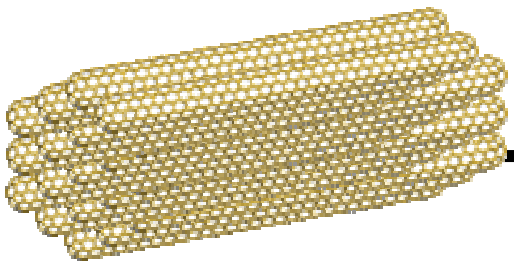


(From Delaney et al., Science 1998)


Field emission display
Aladdin's
Conductive composite
Secondary battery
SAMSUNG
Li-ion
Dispersion
Fuel cell & Hydrogen storage
PEMFC Mass Transit
Supercapacitor
Ultracapacitors
Structural composite
Terabit memory device

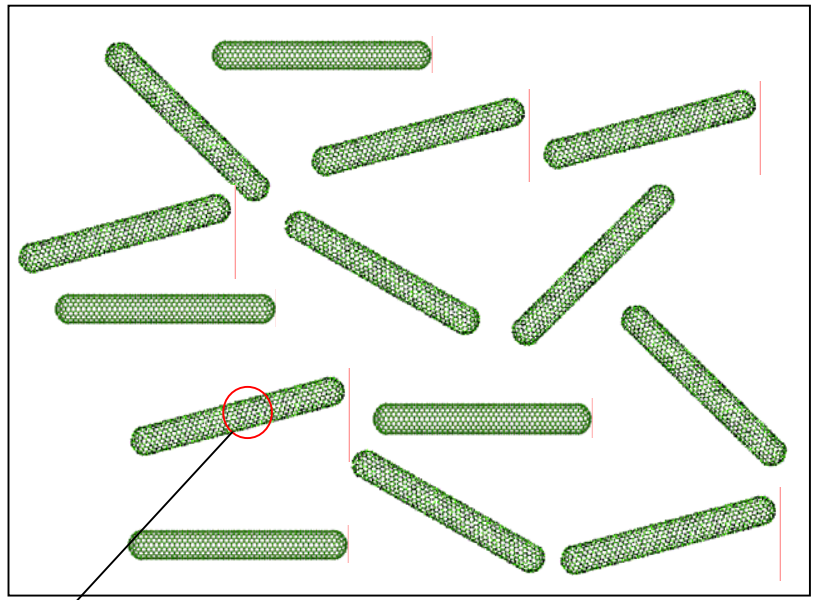
Sonication effects

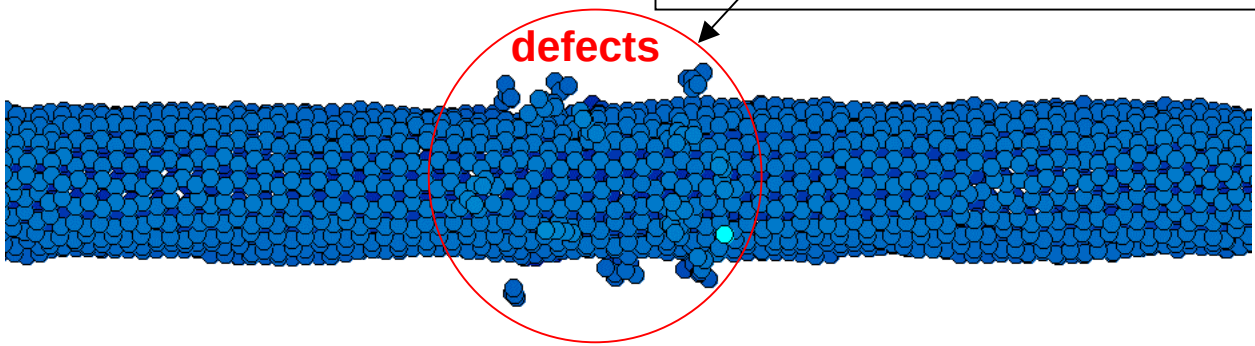
Nanodispersed SWCNTs



Rope of SWCNTs

Sonication





Sonication can induce defects on SWCNTs.

How much and what methods?

Motivation

Methods for macro- & nano-dispersion?

- Choice of solvents
- Surfactants such SDS, NaDDBS in water
- DNA ….
- Organic solvents such as DMF, THF, DCE..
- Ethanol
- Acid treatments…

- Choice of sonication conditions
- sonicator type (bath type, tip type)
- sonication power
- sonication time
- sonication frequency
- tubes types (SW, DW, MW)

Ultrasonic treatment

- Output frequency : 20 kHz
- Output maximum power : ~ 700 W
- Used CNTs : highly purified SWCNTs synthesized by arc-discharge
- CNT concentration: 20 mg in 10 g of ethanol
- Used sonication power : 200 W, 300 W, 400 W, 500 W
- Sonication time: up to 120 min

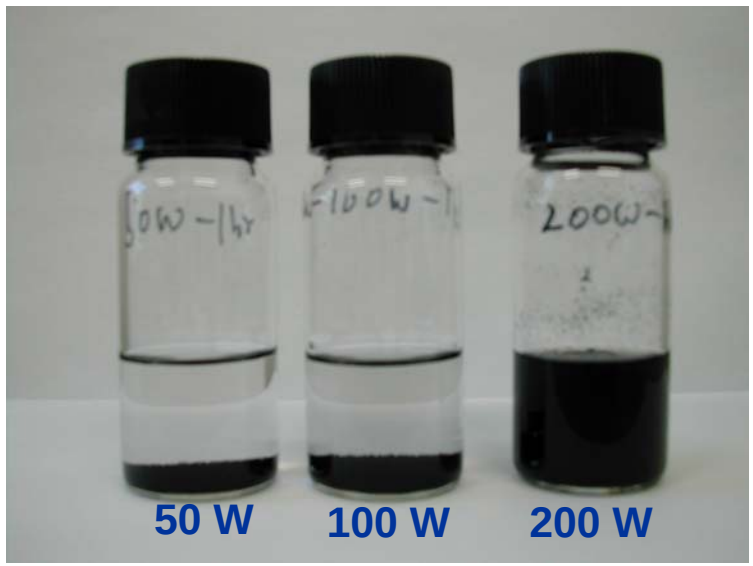


Photo image of sonicated CNTs at 50~200 W for 60 min after one day

Characterization tools

- Raman spectroscopy

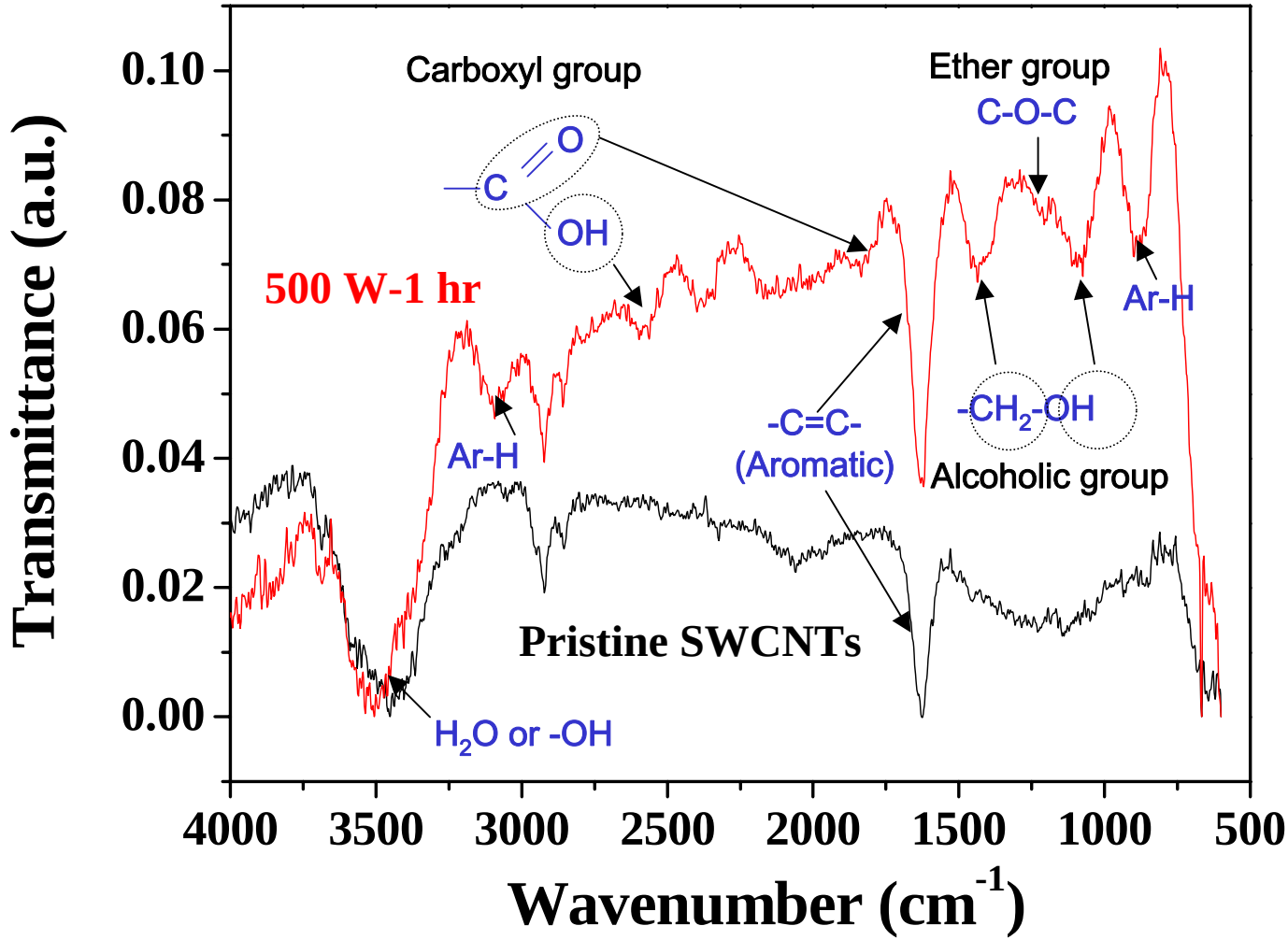
  : excitation energy (514, 633, 785, 1064 nm)

  - G band
  - Radial breathing mode (RBM)
  - D band
  - D' band

- Thermogravimmetric analysis (TGA)

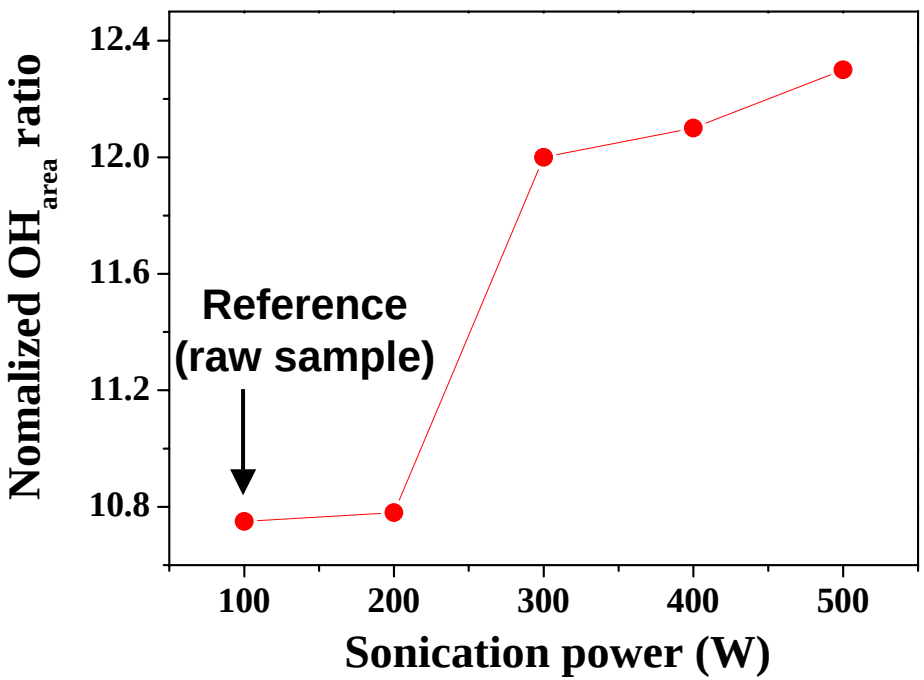
  - Remnants after 1000 ^{o}C: metal oxides
  - Correlation with Raman for defect generation?

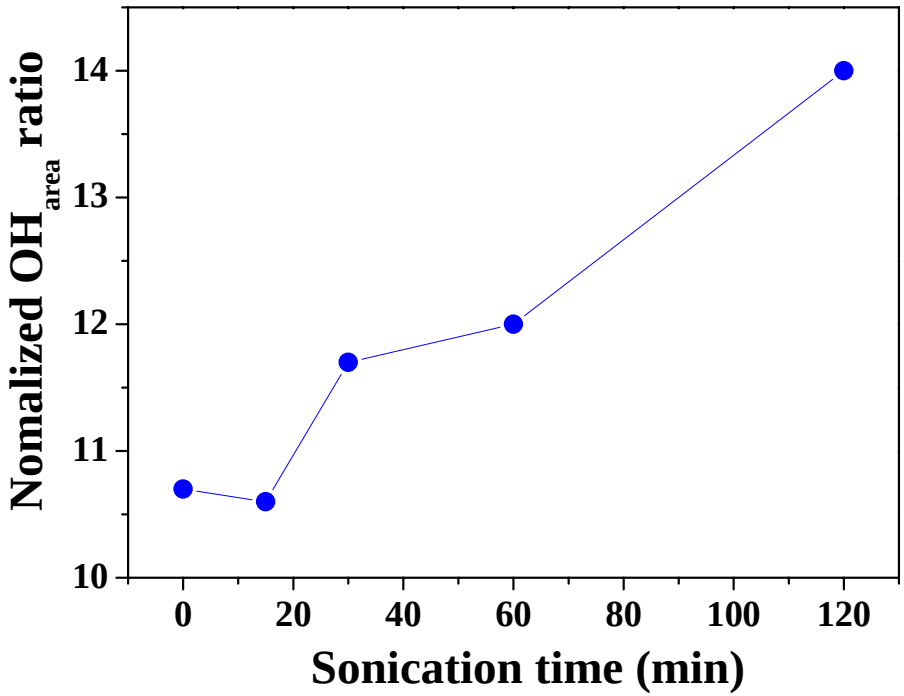
How to identify defect concentration generated by sonication?



Defects generated during sonication were functionalized by OH group.

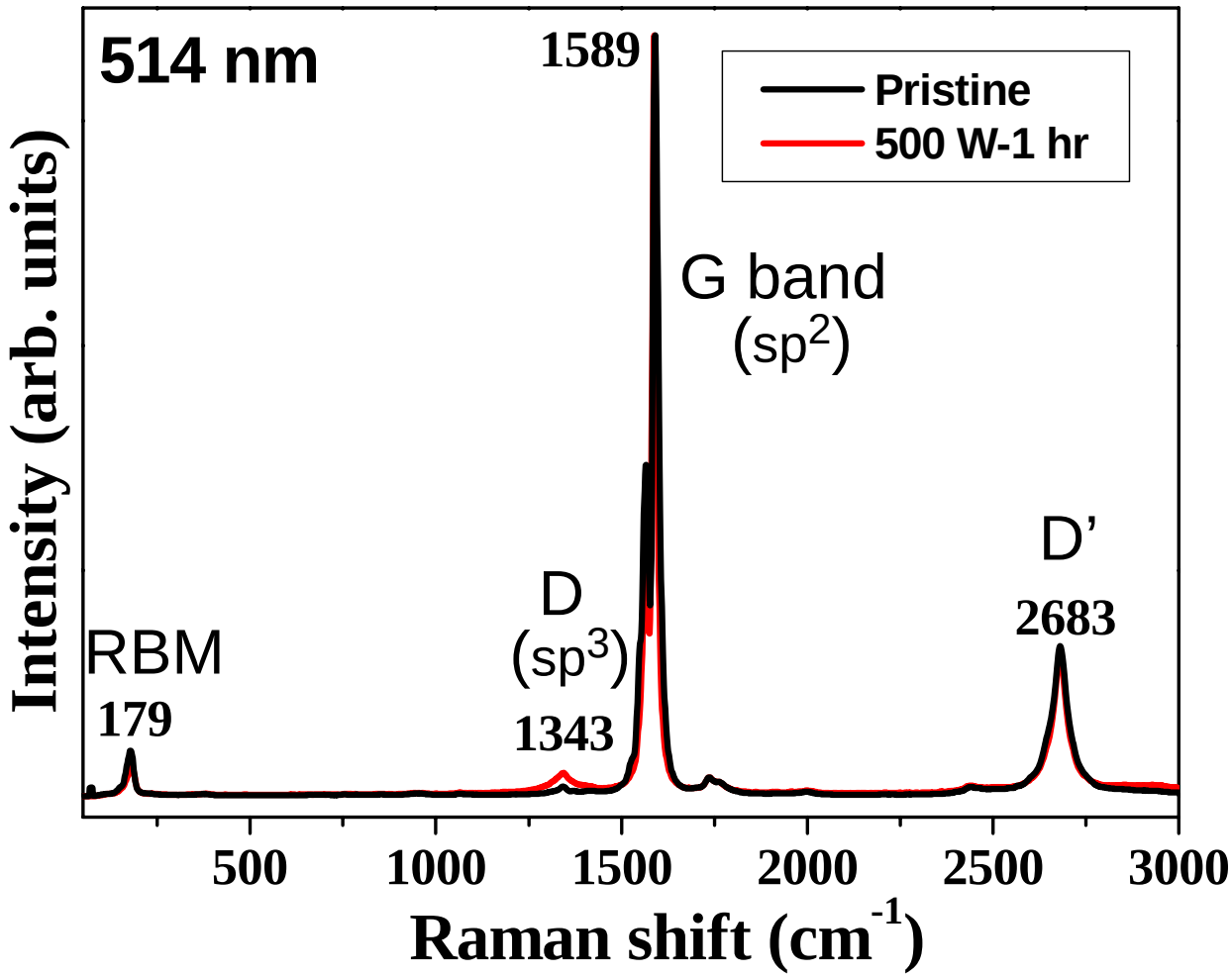
Areal OH band near 3500 cm^{-1}





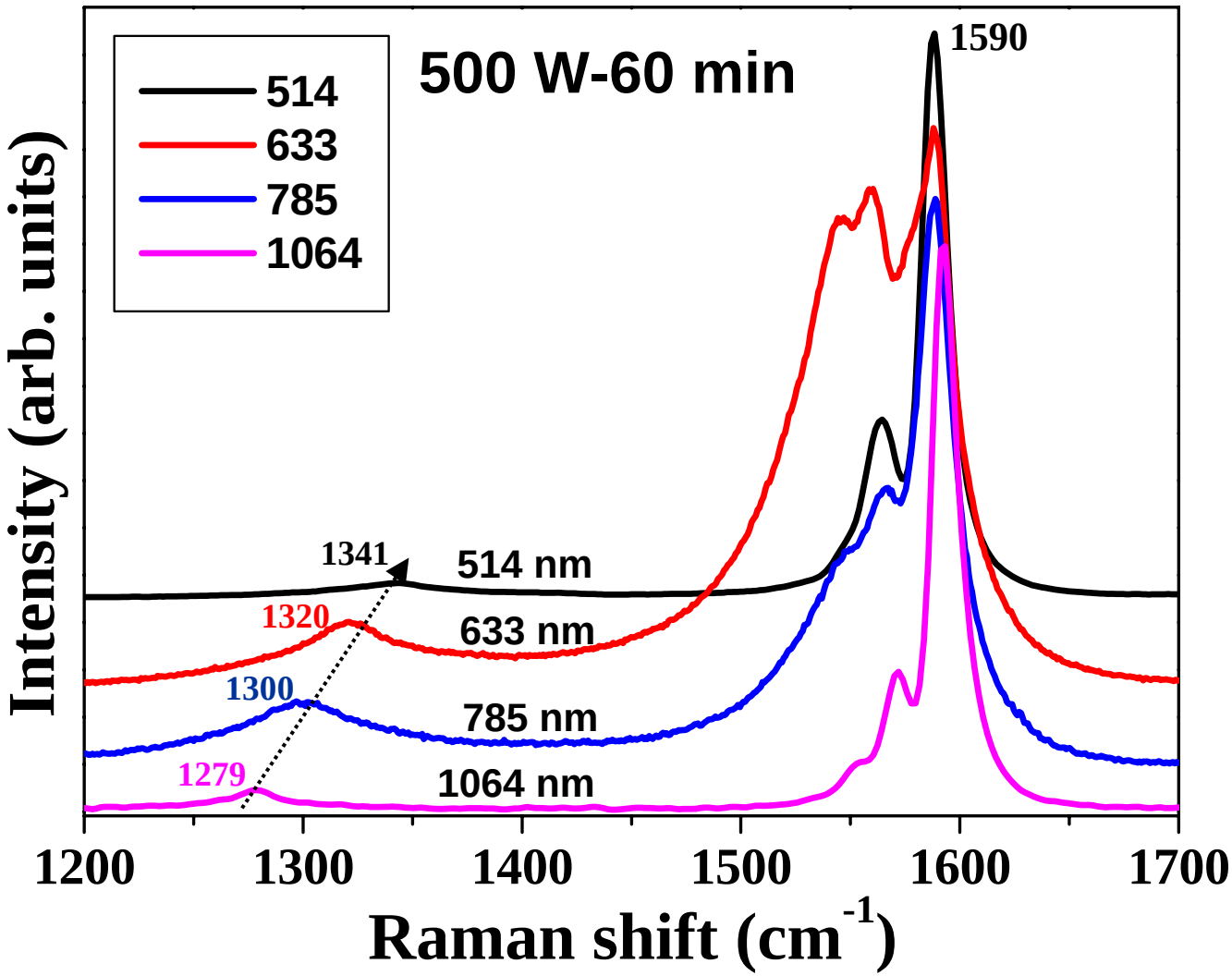
- Integrated area of OH peak will give information for defect concentration.
- These curves will be a guideline in identifying validity of Raman spectra and TGA approaches in assessing the defect formation.

Raman spectrum at 514 nm



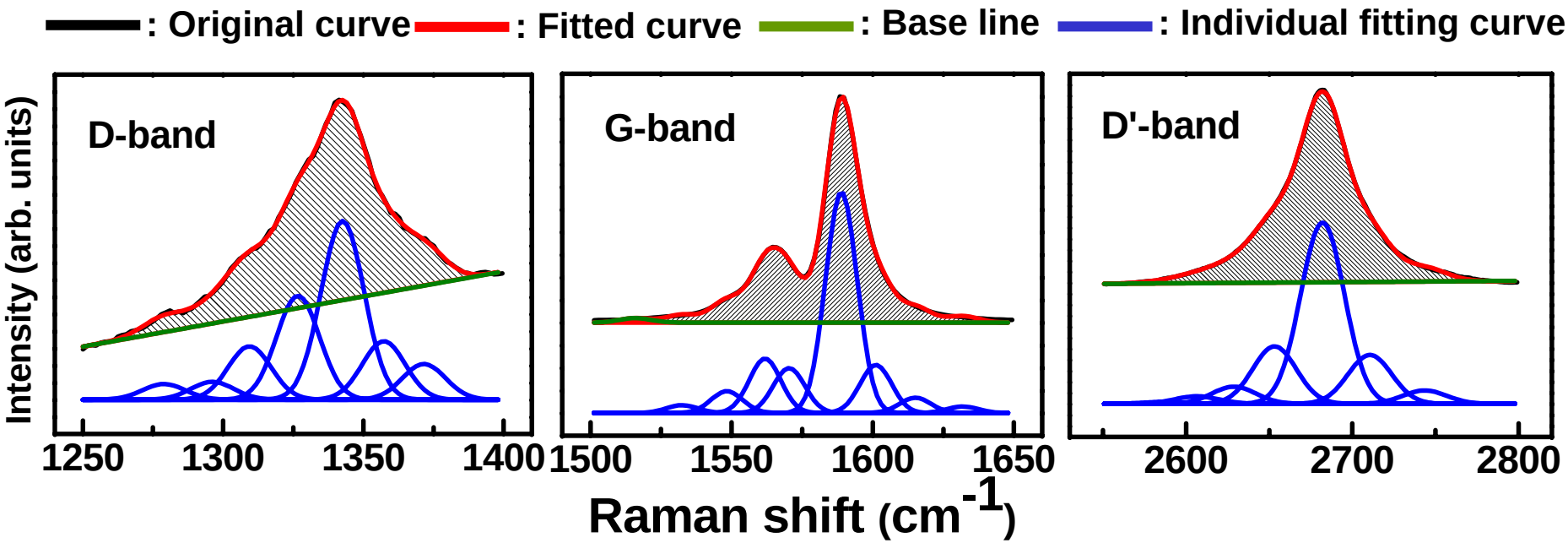
- Which band represents the defect formation by sonication?
- In what forms? D/G, D, D'? intensity or integrated area?

Peak shift of D-bands as a function of excitation energy in Raman spectra



Calculation of D/G

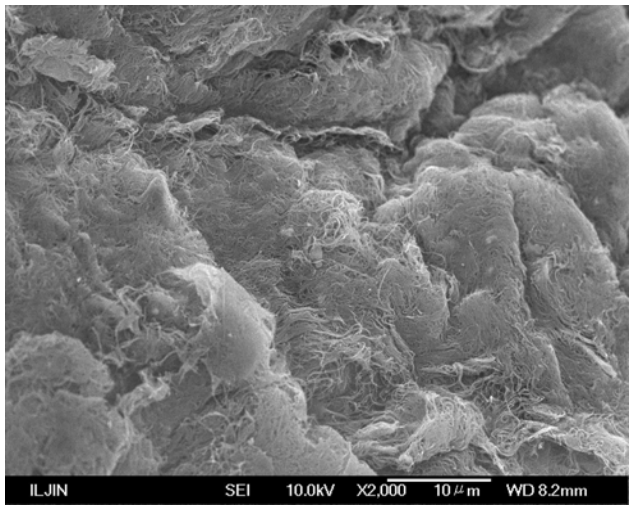
$$D/G_{area} = \frac{D_{area}}{G_{area}} \text{ (Area ratio)} \qquad D/G_{int} = \frac{D_{int}}{G_{int}} \text{ (Intensity ratio)}$$

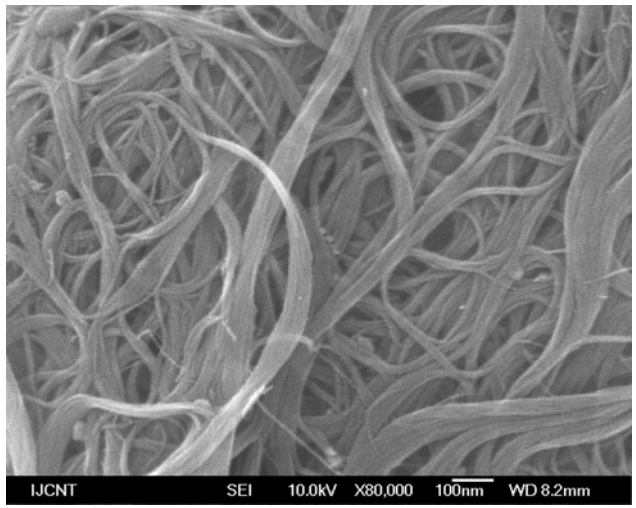


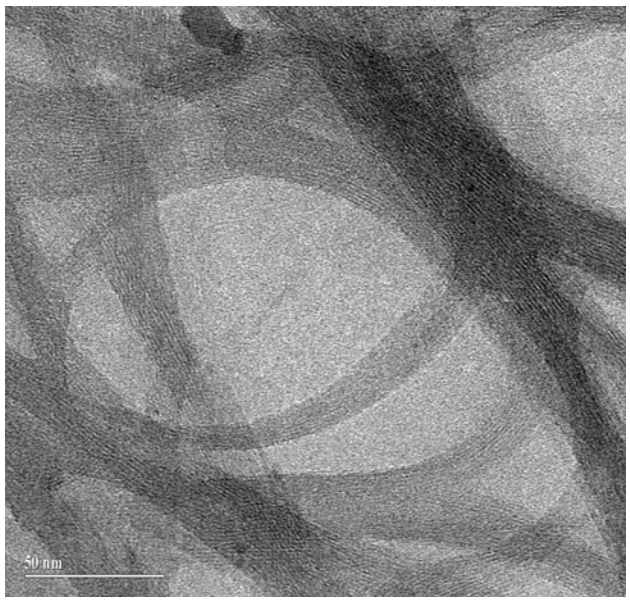
Area ratio : fitted D-band area / fitted G-band area

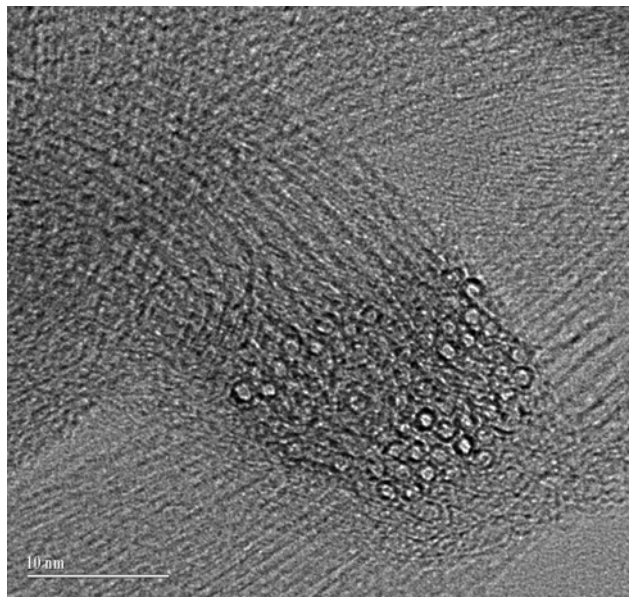
Intensity ratio : maximum peak of D-band/maximum peak of G-band

SEM & TEM images of purified SWCNTs synthesized by arc discharge

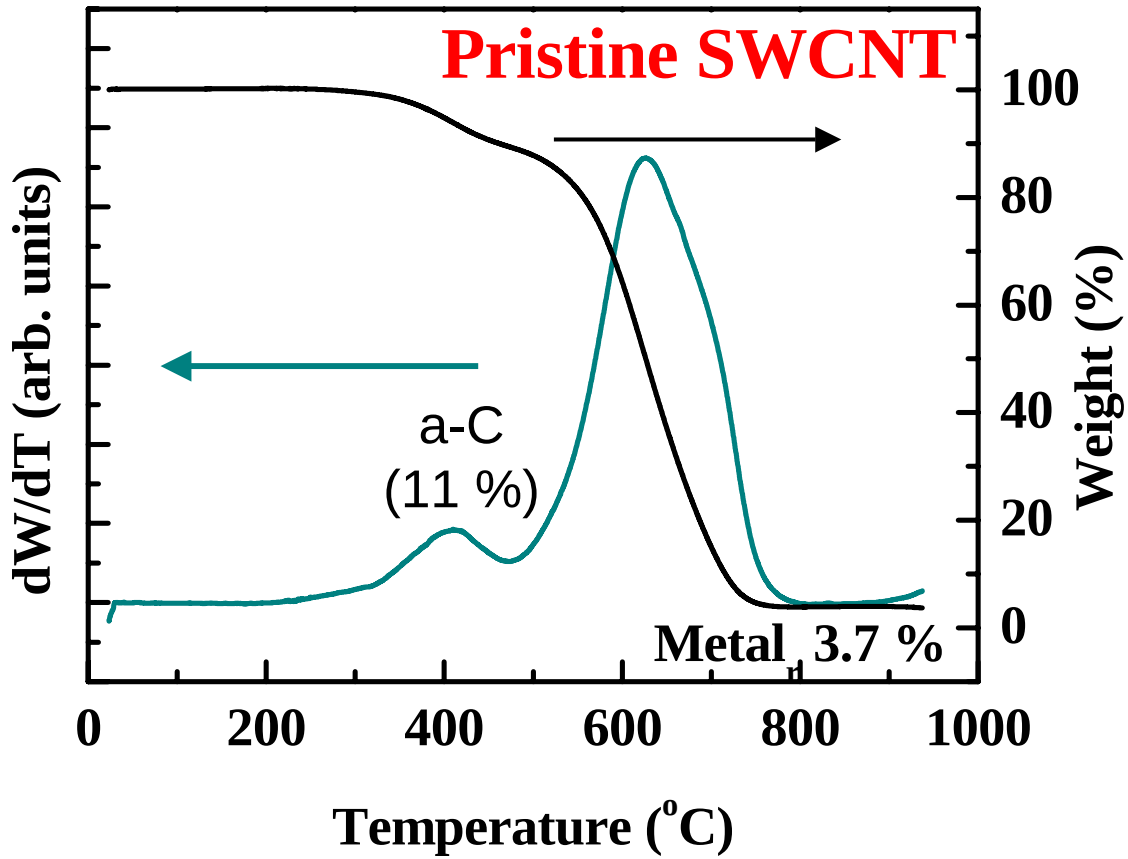




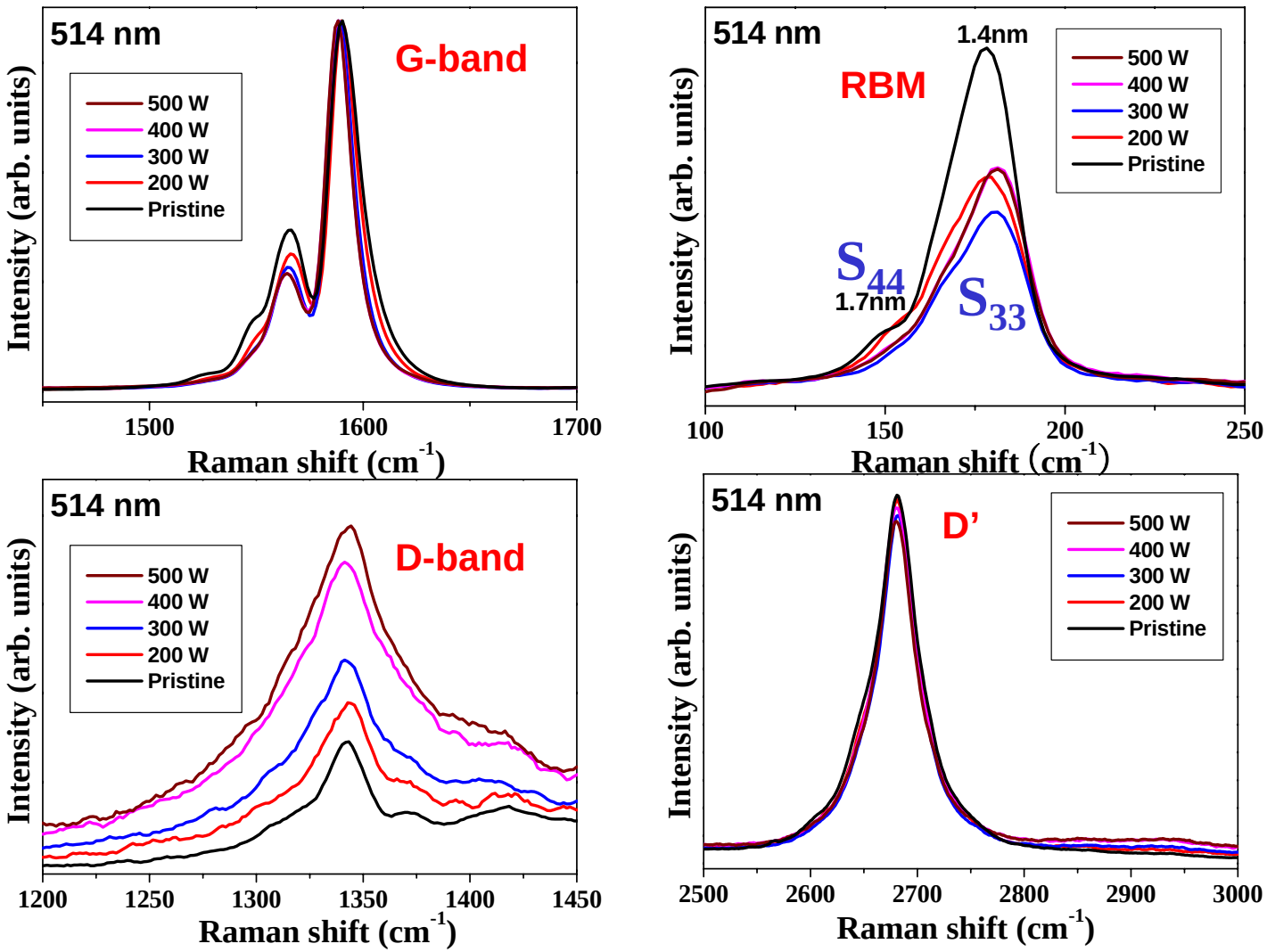




TGA of purified arc-discharge sample

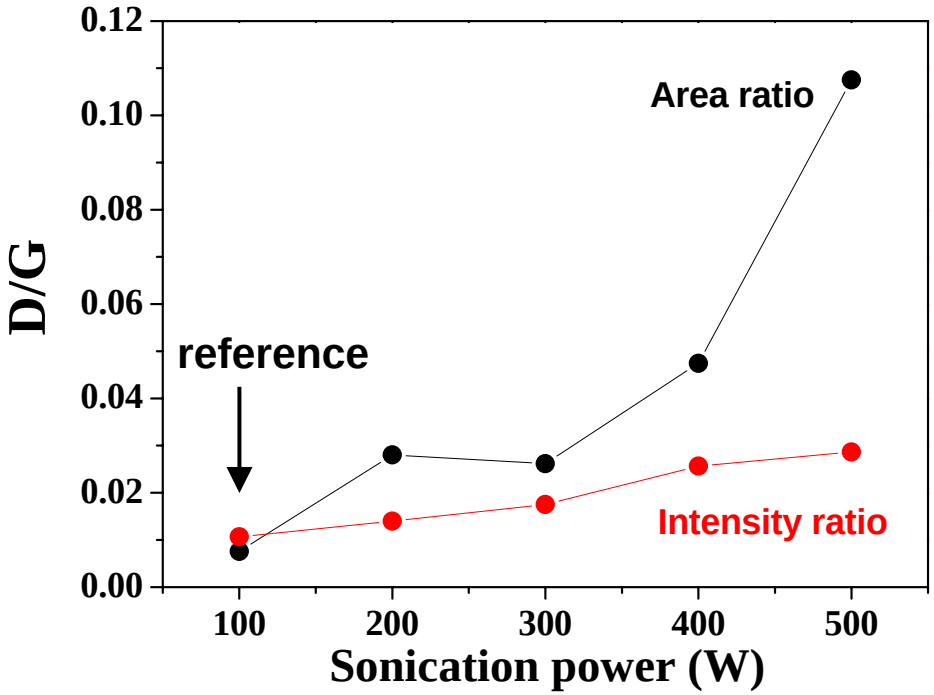


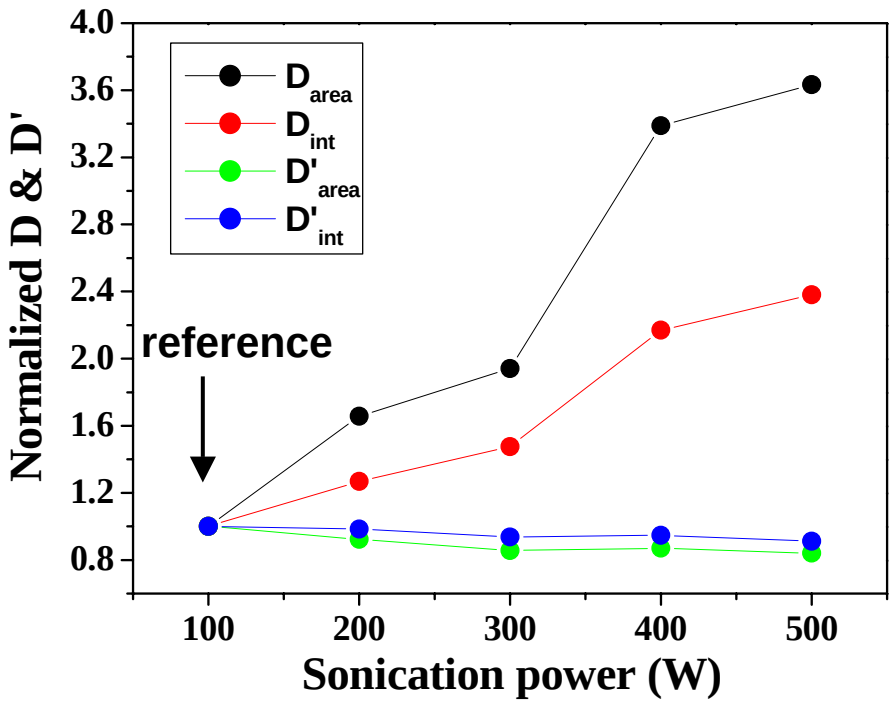
Raman spectra: Sonication power at 514 nm



D-band increases consistently with sonication power.

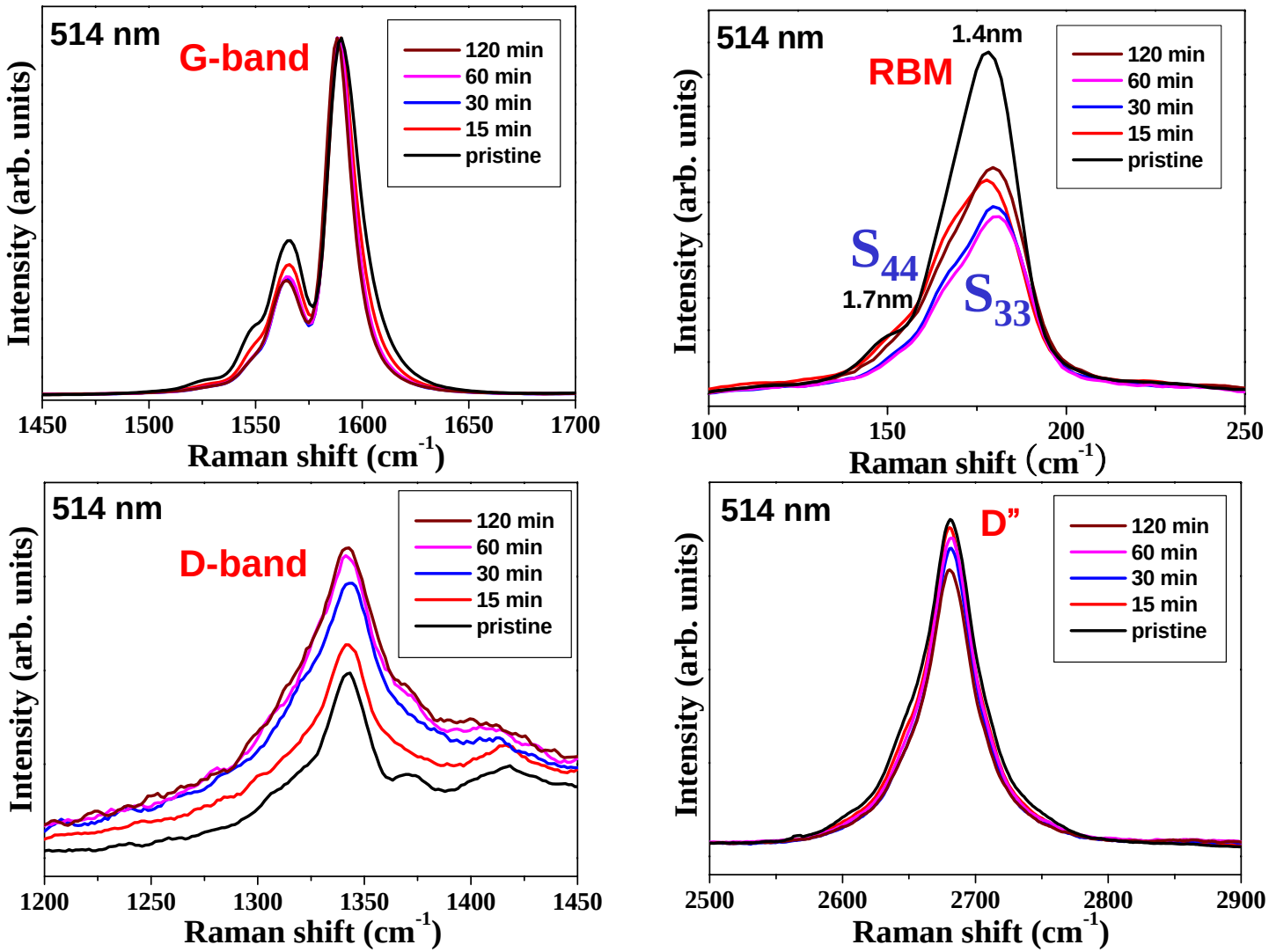
D-band dependence on sonication power



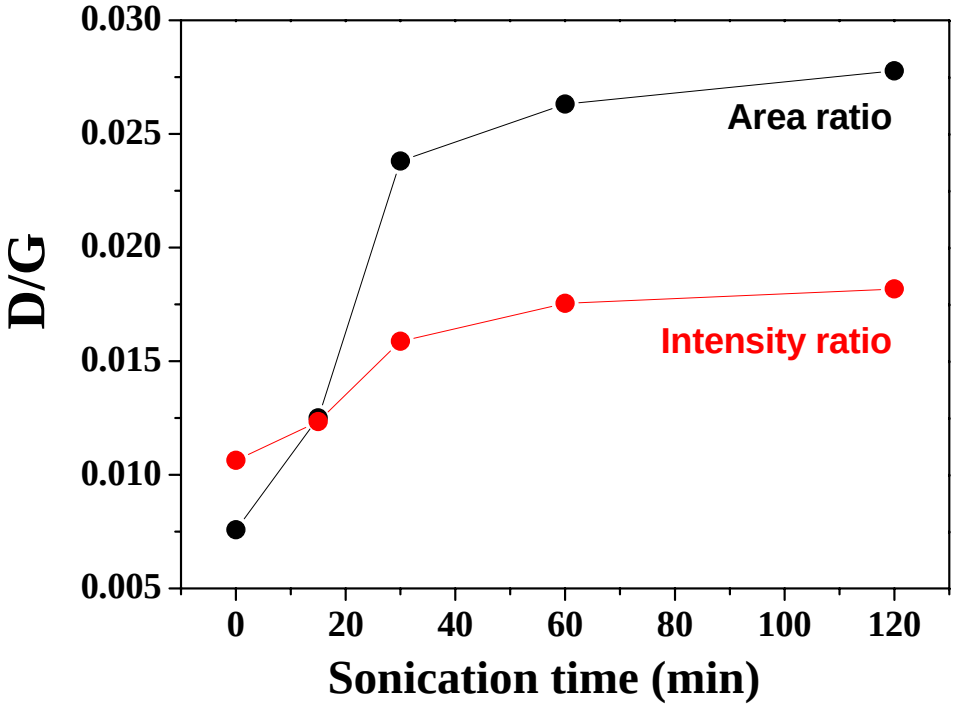


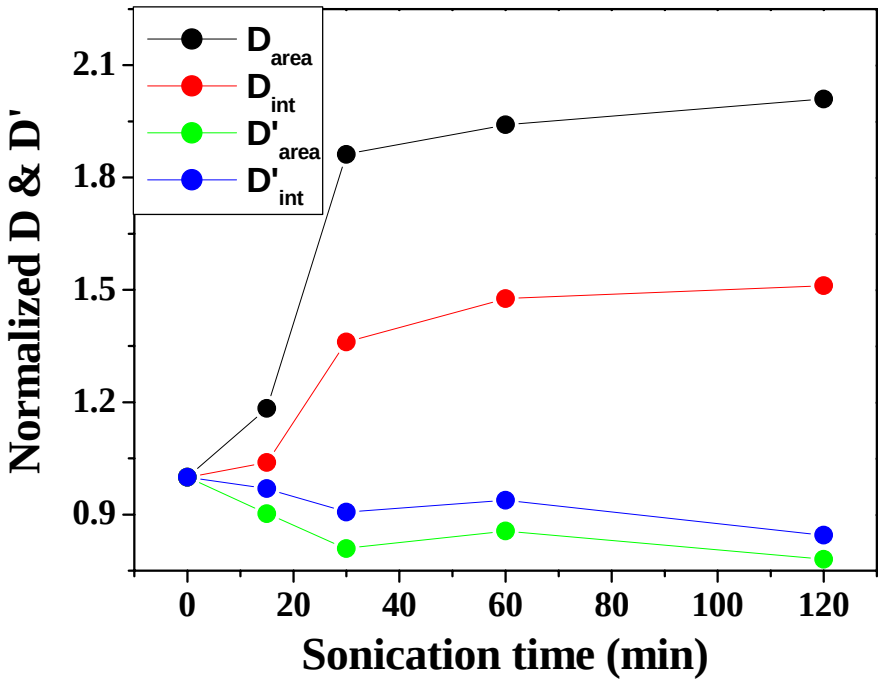
- Both area and intensity of D/G and D band are consistent with each other.
- D/G_{area} changes more rapidly than D/G_{int} with increasing sonication power.
- D' decreases slightly and may not be a good measure of defect formation.

Raman spectra: Sonication time at 300 W



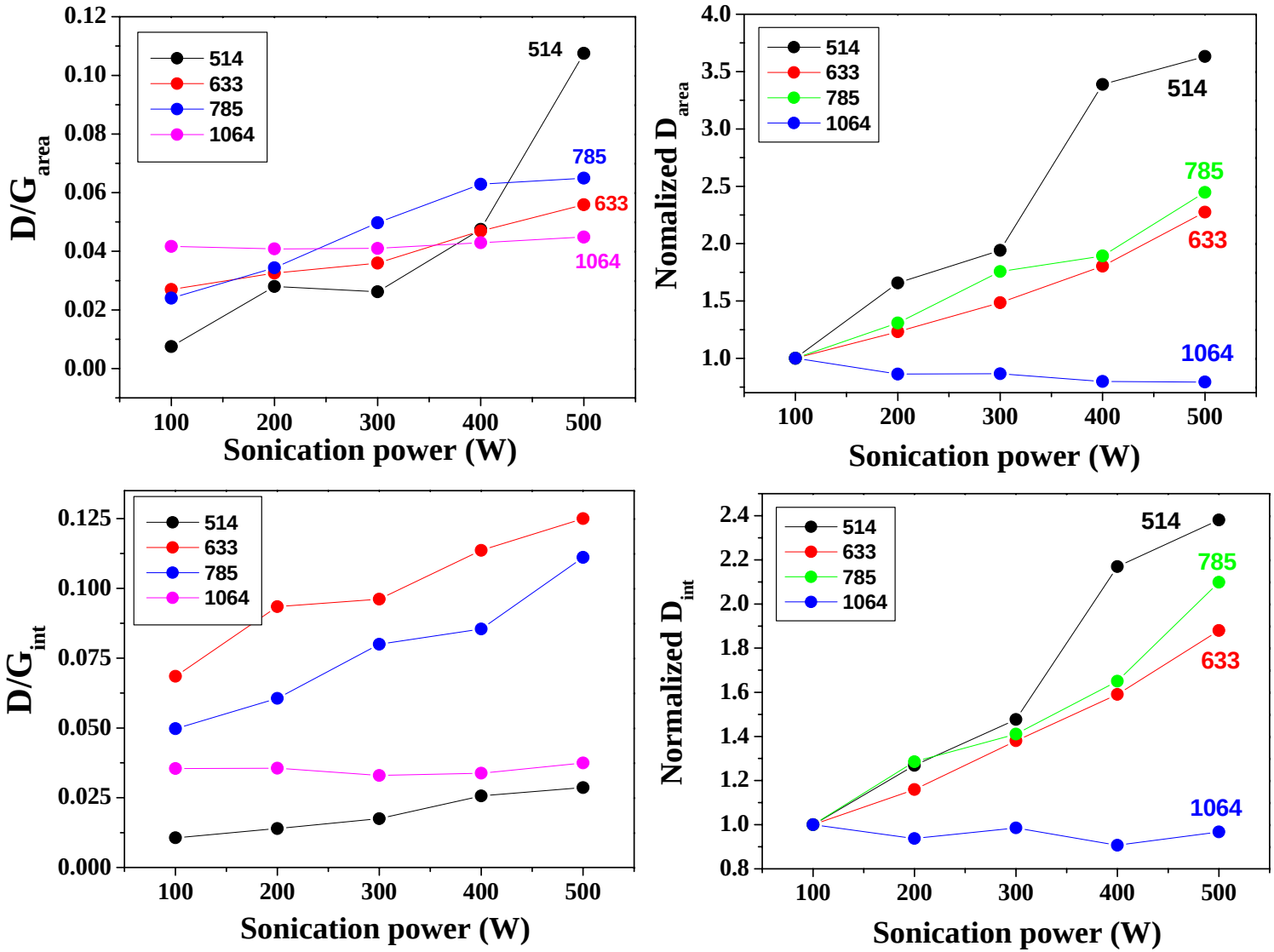
D-band dependence on sonication time



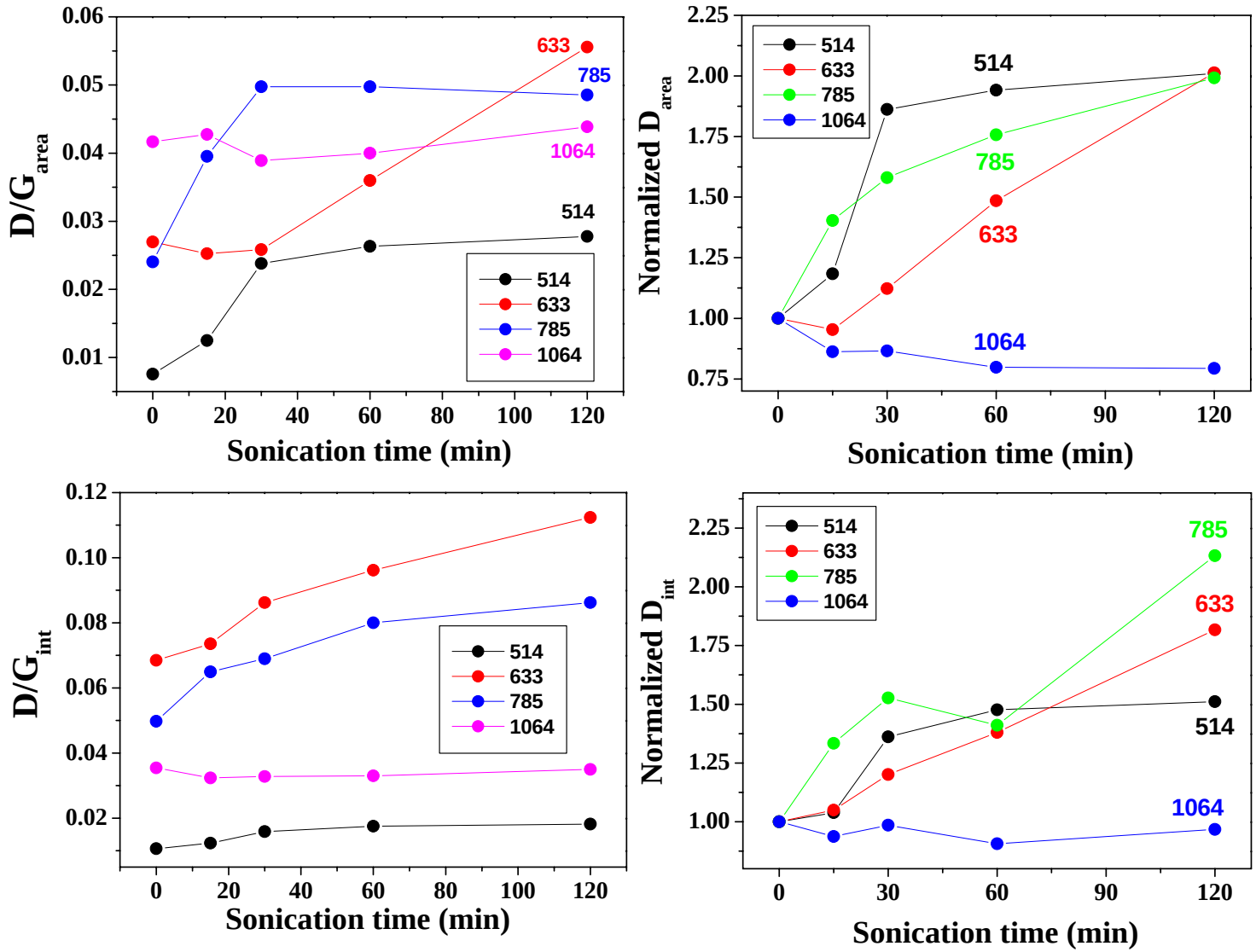


- Defect generation saturate at about 30 min of sonication time at 300 W.
- D/G_{area} (D_{area}) change more rapidly than D/G_{int} (D_{int}) with increasing sonication time.
- D' decreases slightly and may not be a good measure of defect formation.

D/G_{area} in various wavelengths as a function of sonication power



D/G in various wavelengths as a function of sonication time



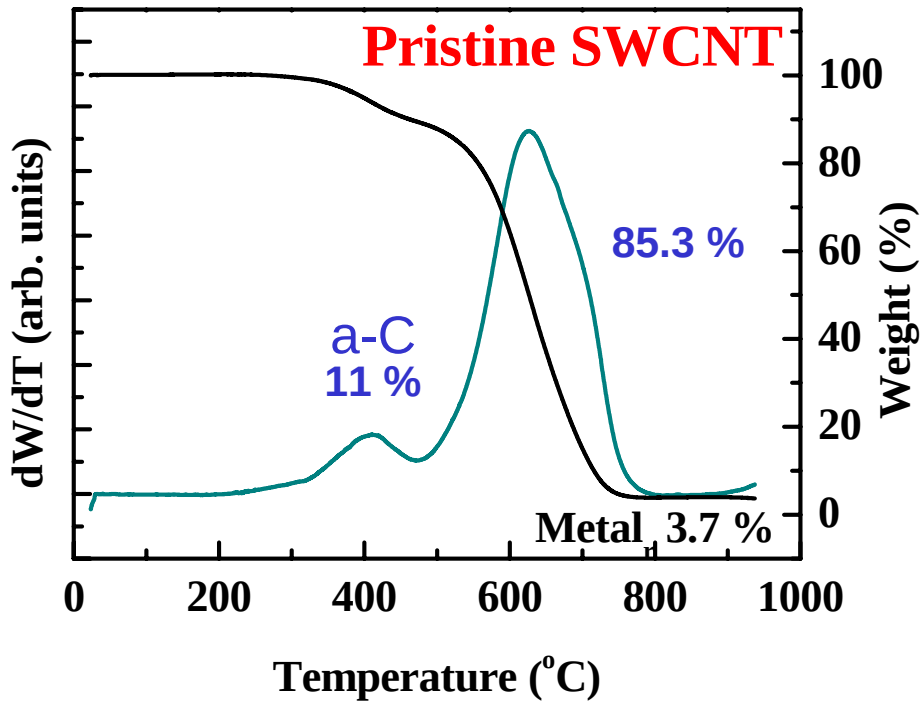
Summary of D-band analysis

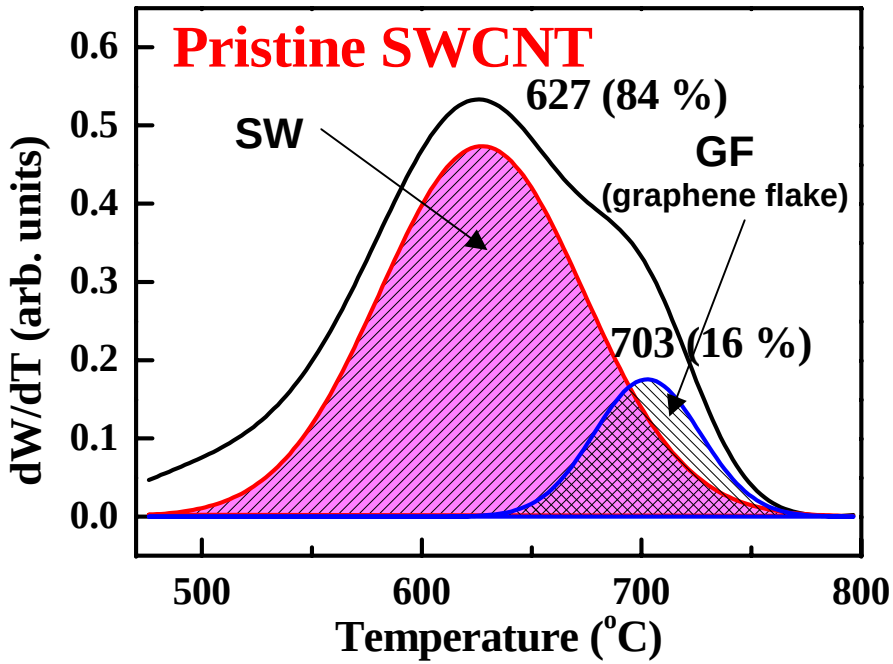
- D-band can represent the defect generation rate during sonication qualitatively similar to FTIR data and perhaps quantitatively with care.
- The best choice in representing defect generation is the intensity ratio of D/G and normalized D peak intensity, for both sonication power and time.
- The increase of D band does not originate from a-C.
- Sonication power generates more defects than sonication time.

Analysis of TGA profile of pristine SWCNTs

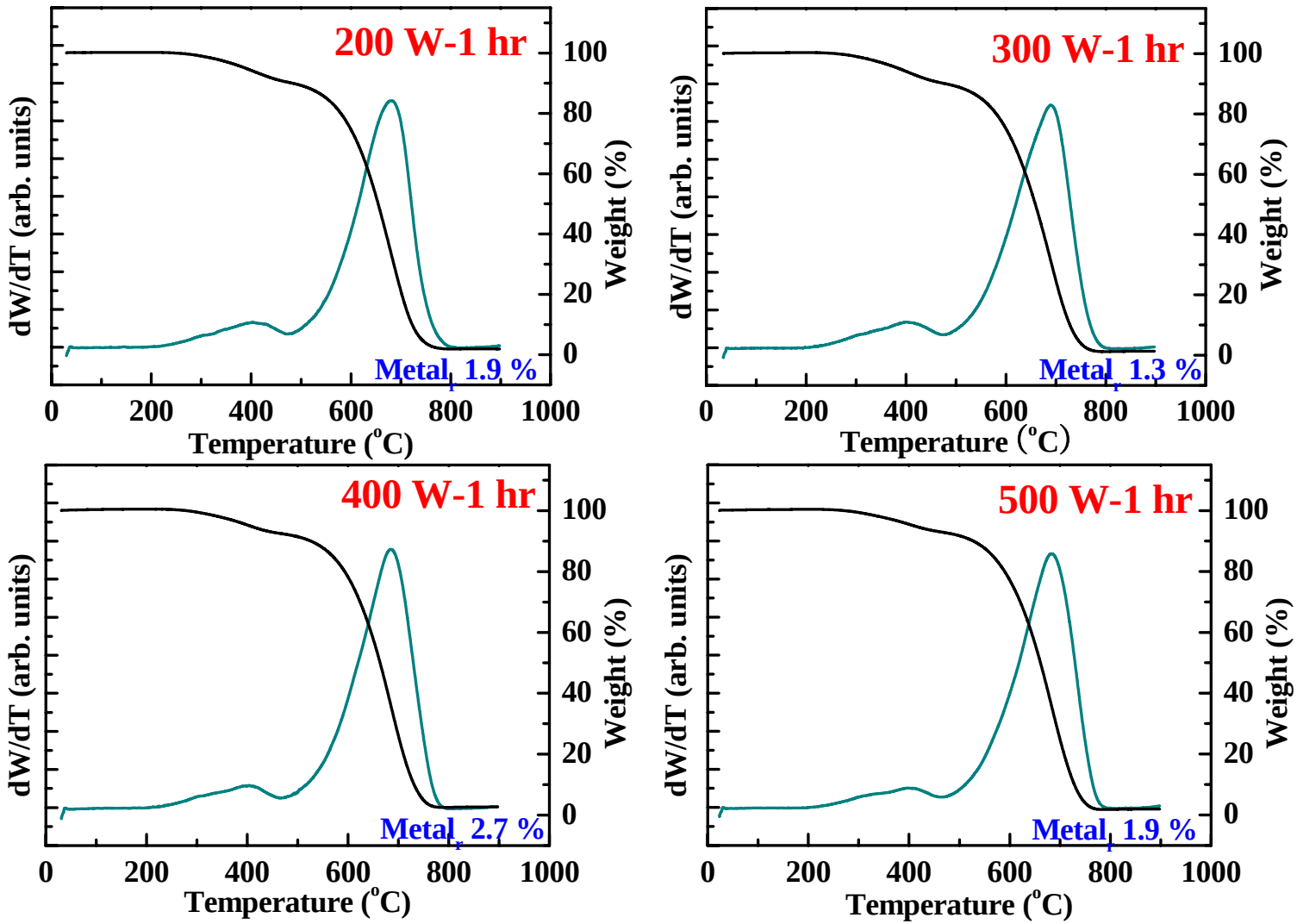
Conditions of TGA measurement

- Pre-desiccate : flowing N_2 @ 200 °C
- Annealing until stable mass was achieved
- Heating rate : 5 °C/min
- Atmosphere : dry air - 99.999% - 100 sccm
- TGA run on 5-6 mg of SWCNTs to 1000 °C

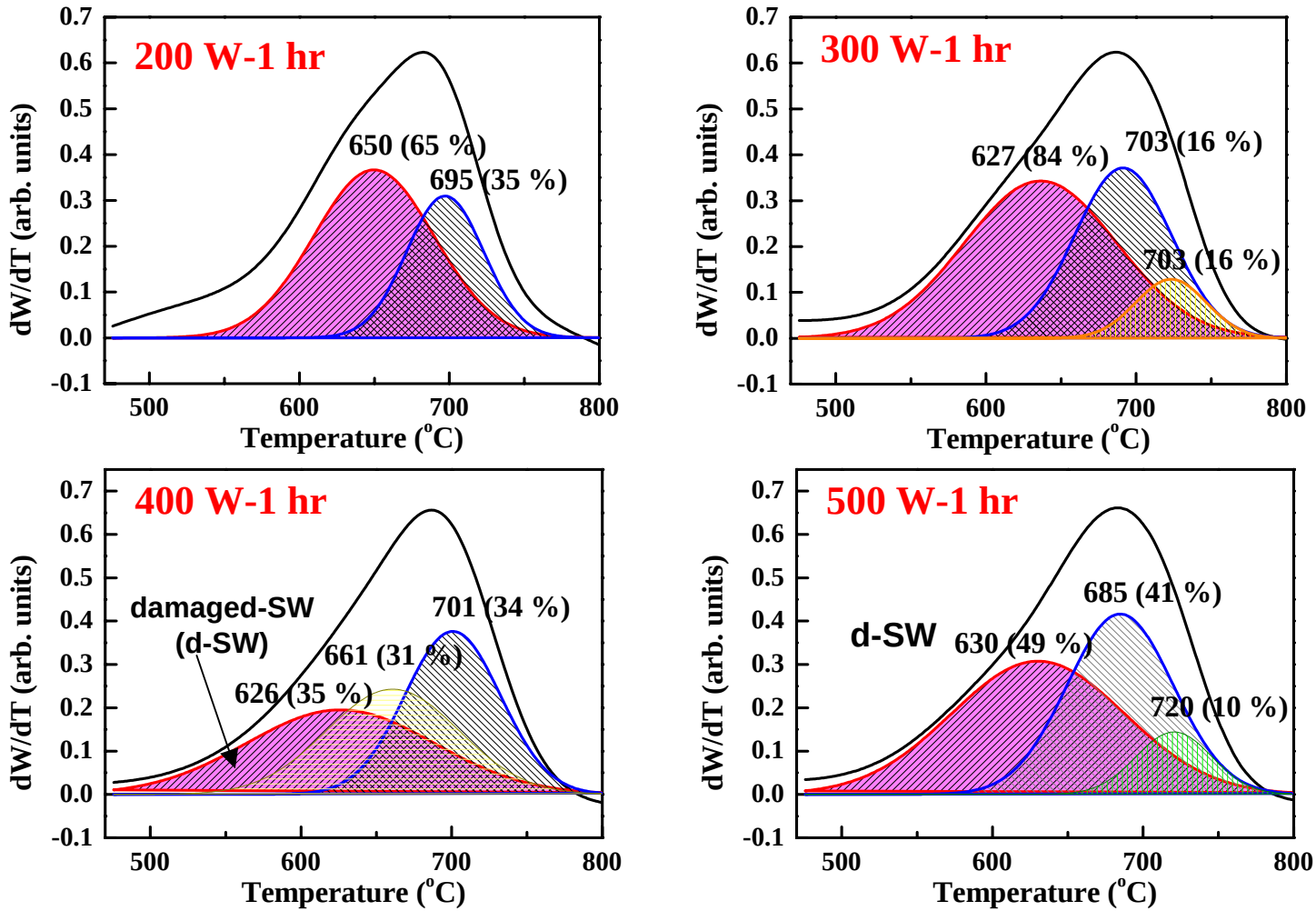




Analysis of TGA profile: sonication power

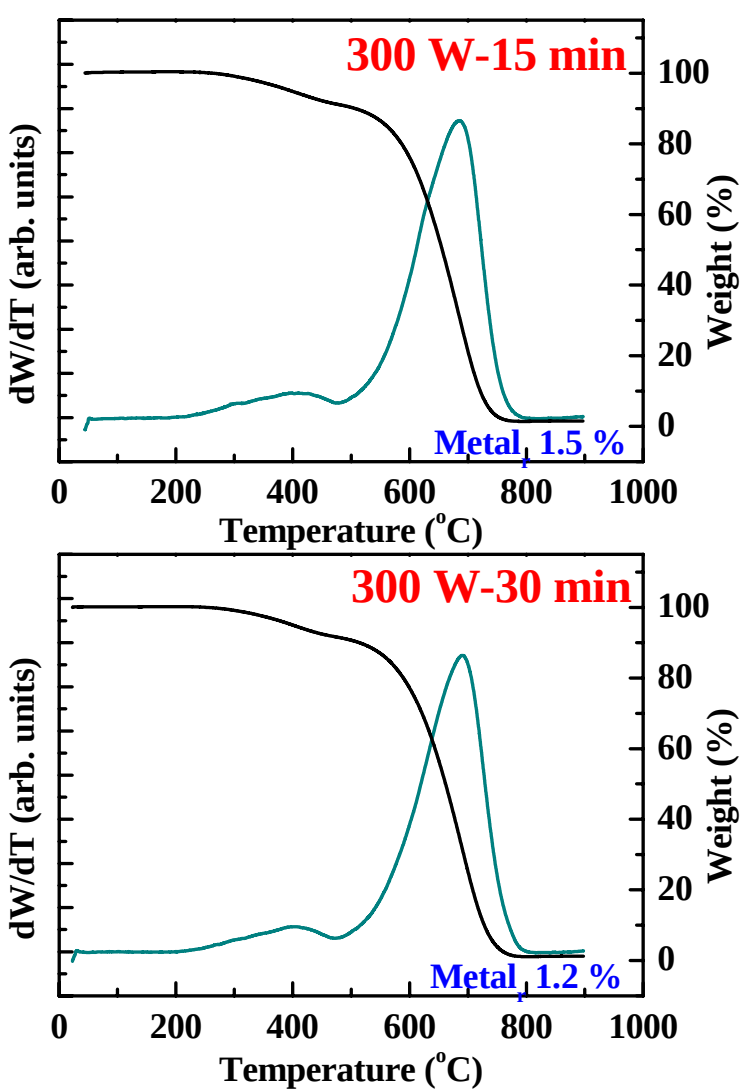


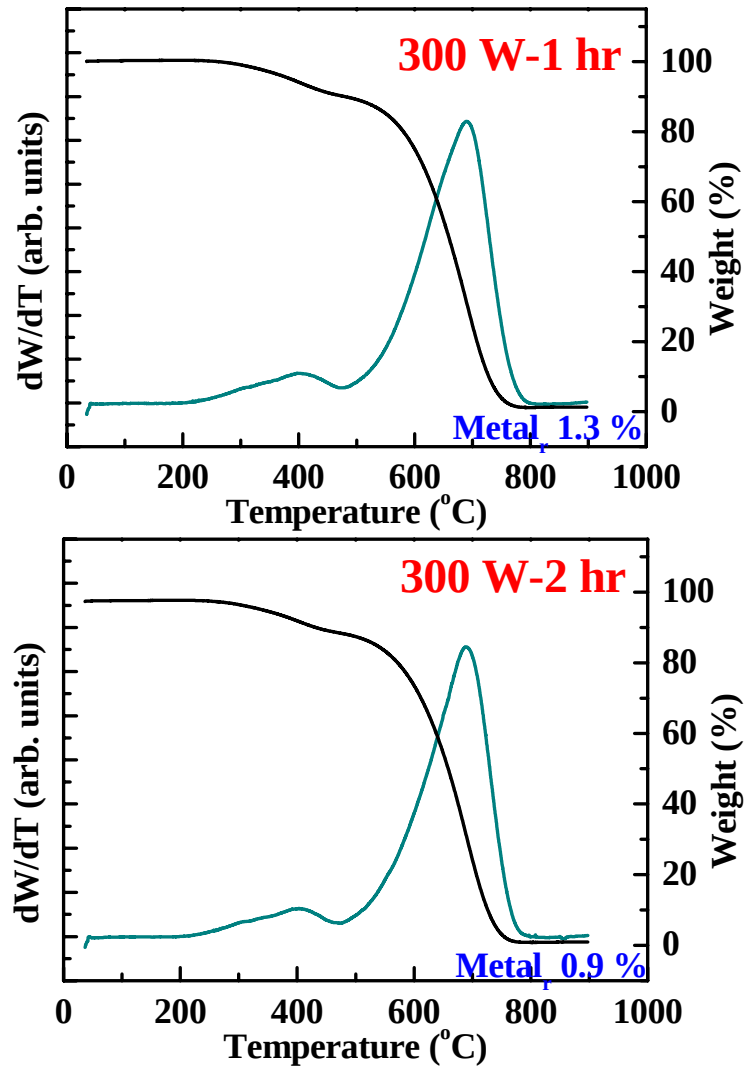
Analysis of TGA profile: sonication power



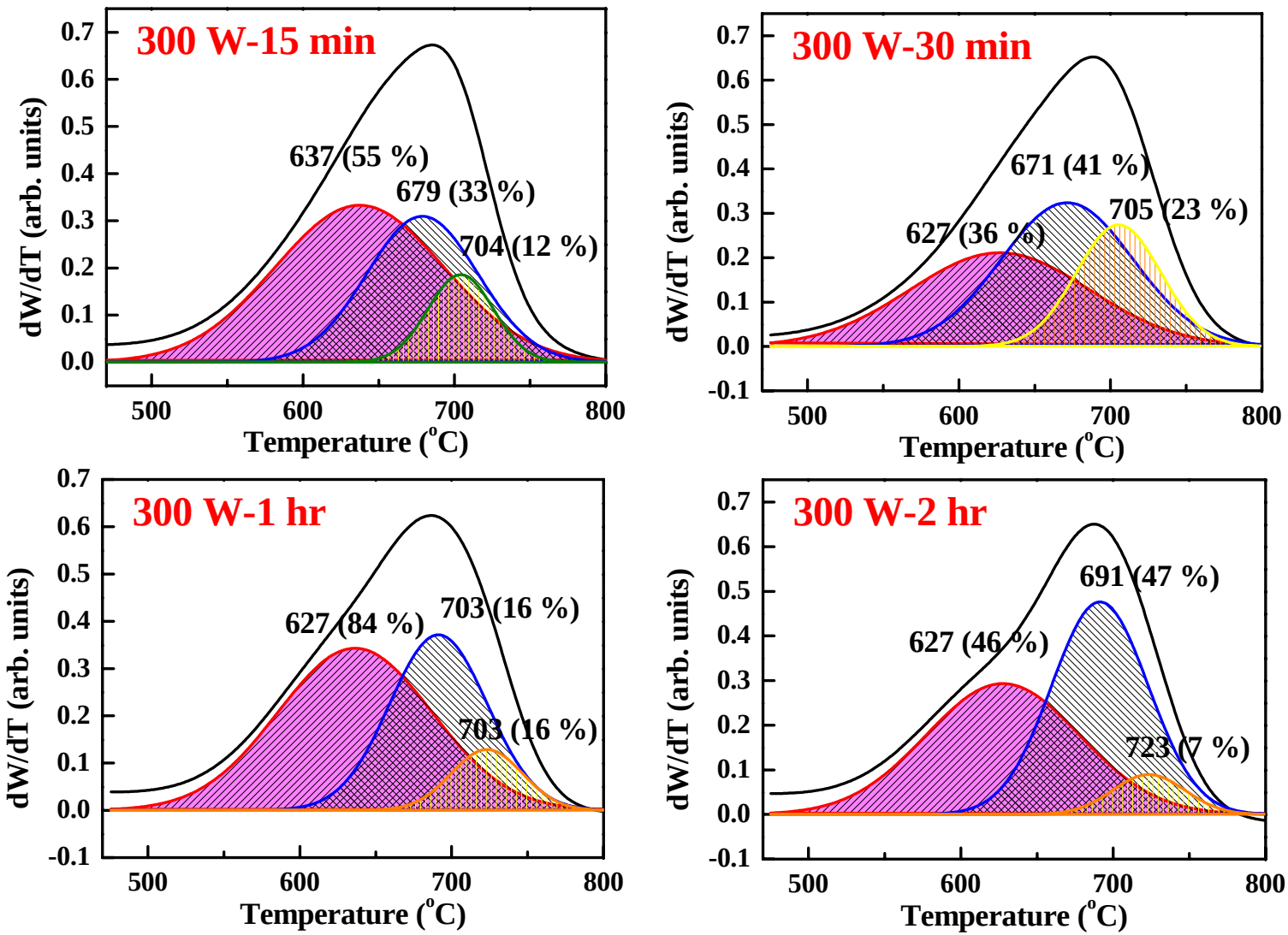
A bump at the lower temperature side is developed with increasing sonication power => damaged SWCNTs??

Analysis of TGA profile: Sonication time

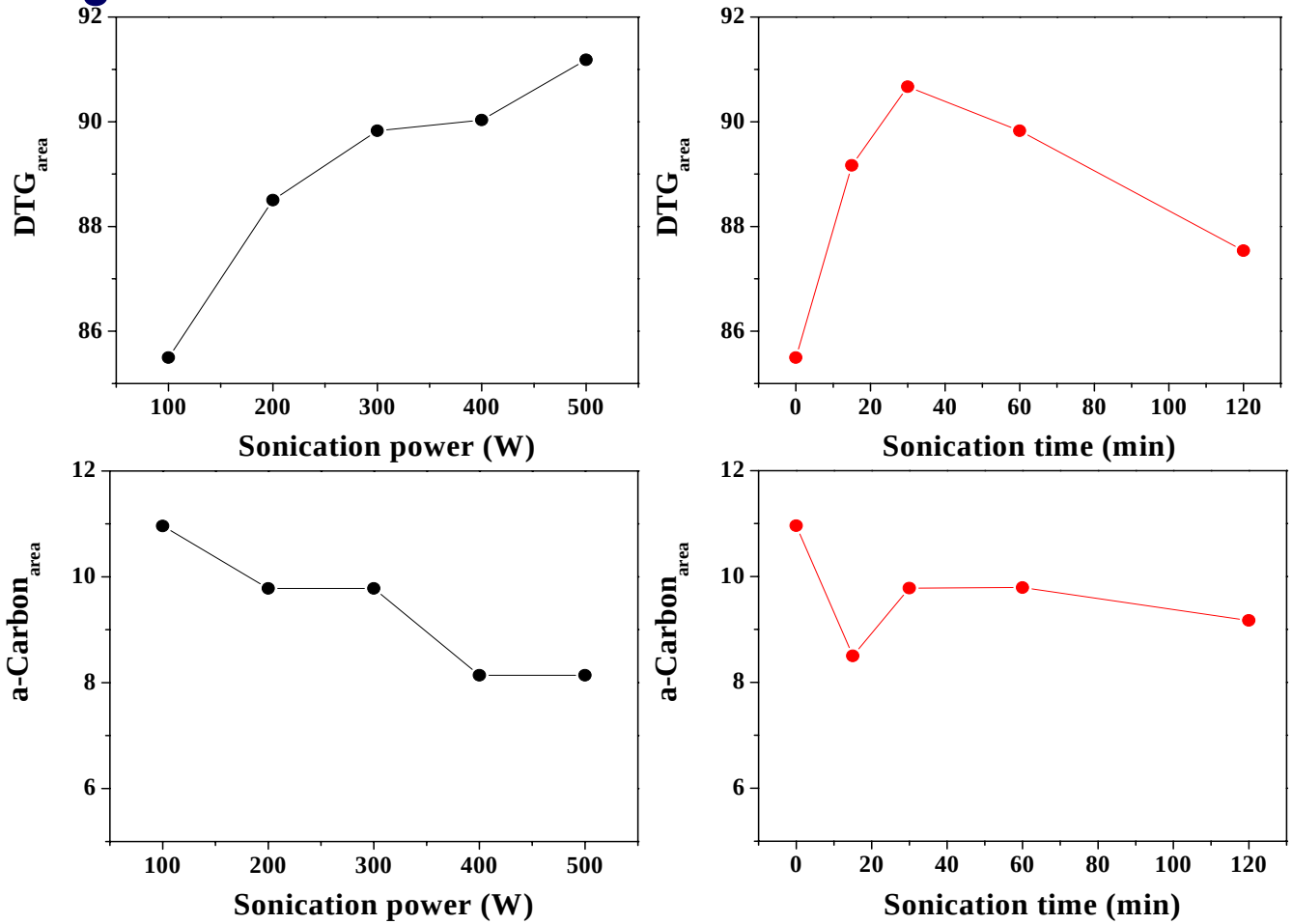




Analysis of TGA profile: sonication time



Integrated area of DTG



- Strong correlation exists in sonication power between areal DTG peak and D-band in Raman spectra but not in sonication time.
- a-carbon does not follow D band in Raman spectra and DTG curve.

Summary

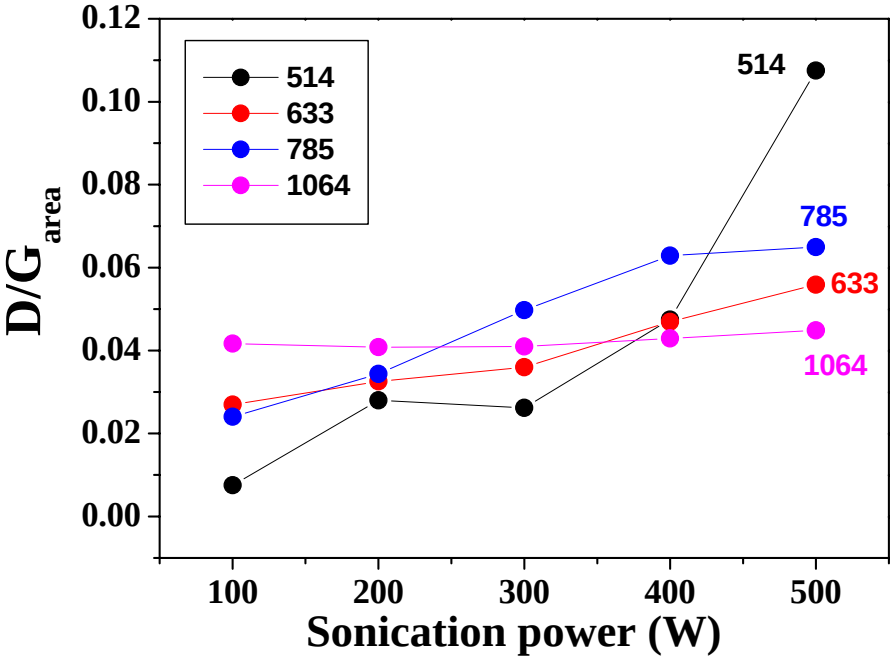
- The intensity of D/G and D-band in Raman spectra can represent the defect generation rate during sonication (power and time) qualitatively.

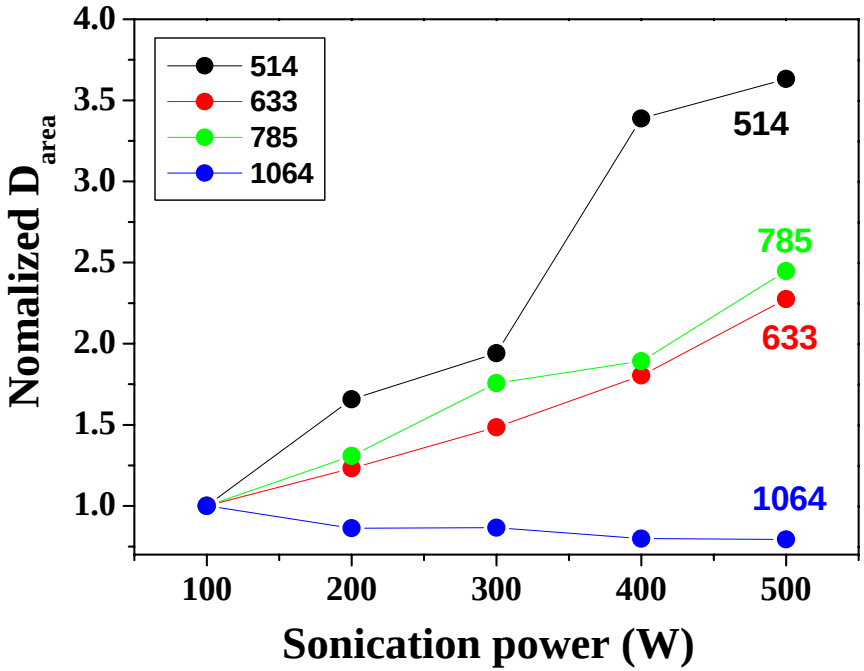
- The integrated area of DTG curve can be a measure of defect formation in agreement with FTIR measurements.

- The change of a-C area in DTG is negligible with sonication and therefore D-band changes do not originate from a-C.

- More detailed analysis of TGA and DTG is required
  - identification of peaks in DTG curve from SW, DW, MW, graphite
  - burning temperature: defects, bundle size, diameter

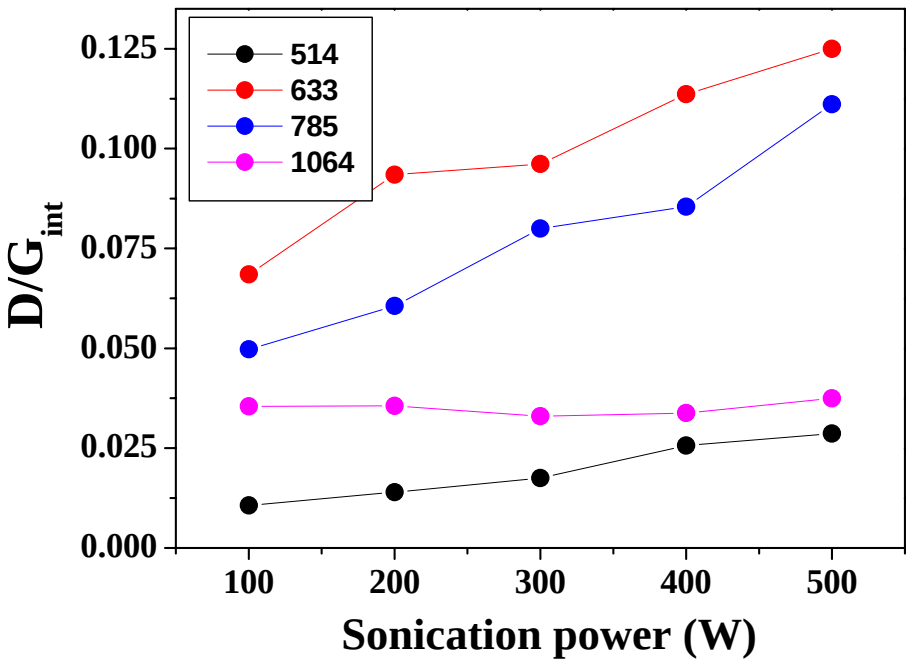
D/G_{area} in various wavelengths as a function of sonication power

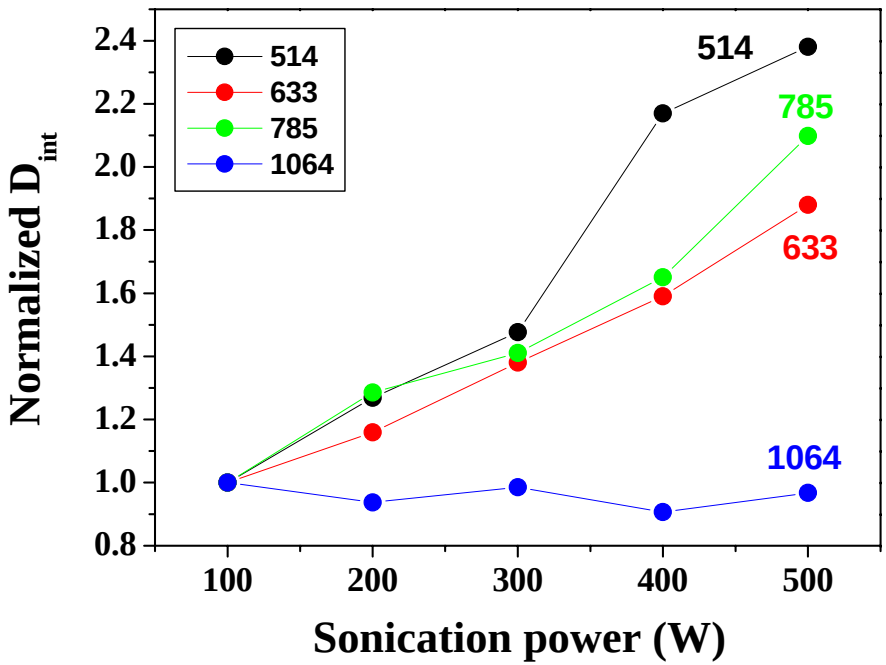




- Both D/G_{area} and normalized D_{area} band show a consistent increase with sonication power except 1064 nm.
- This may come from the different Raman configuration, 1064 nm; FT-Raman, others: micro-Raman

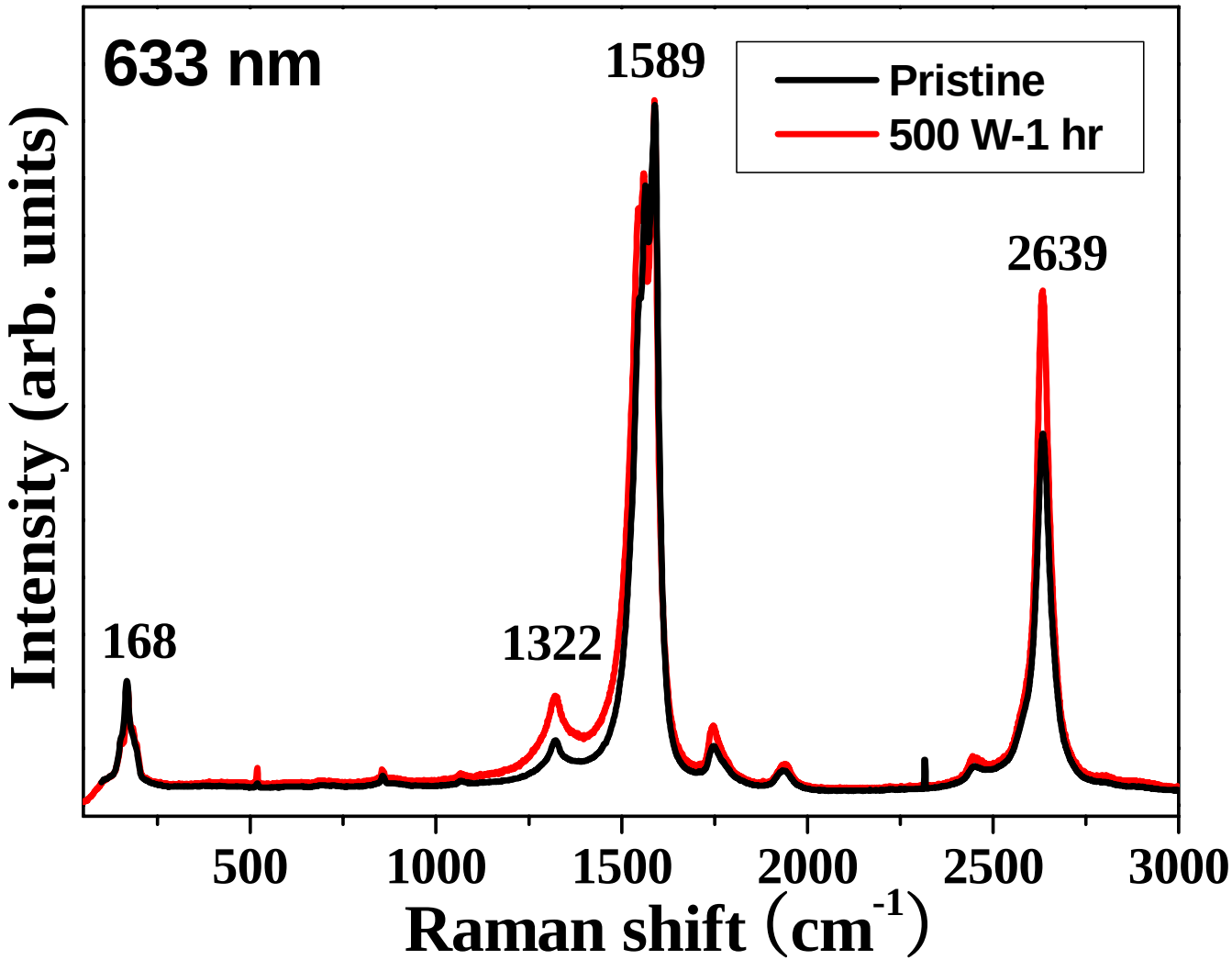
D/G_{int} in various wavelengths as a function of sonication power



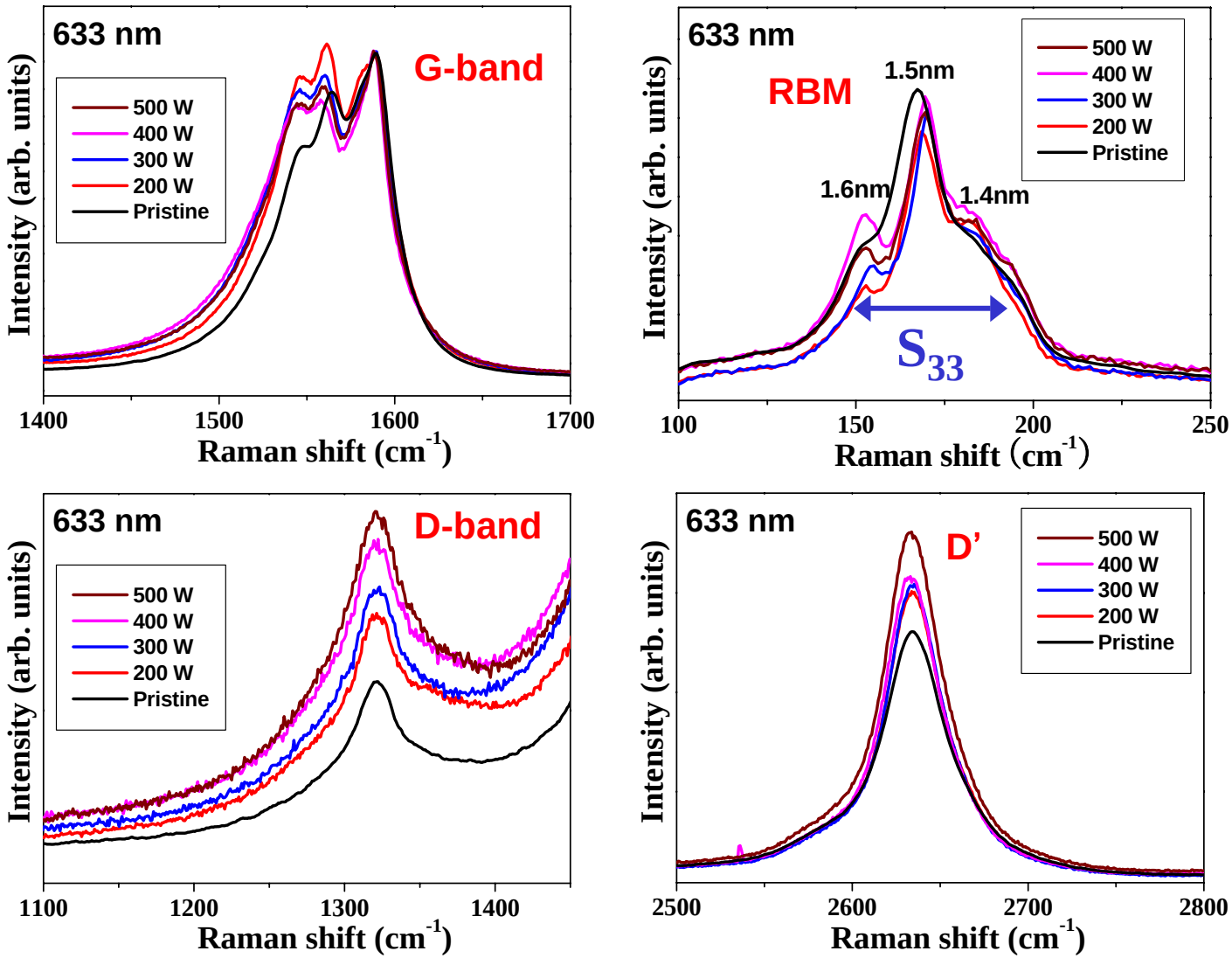


- $D/G_{intensity}$ and normalized $D_{intensity}$ represent stronger correlations than D/G_{area} and normalized D_{area} for all wavelengths except 1064 nm.

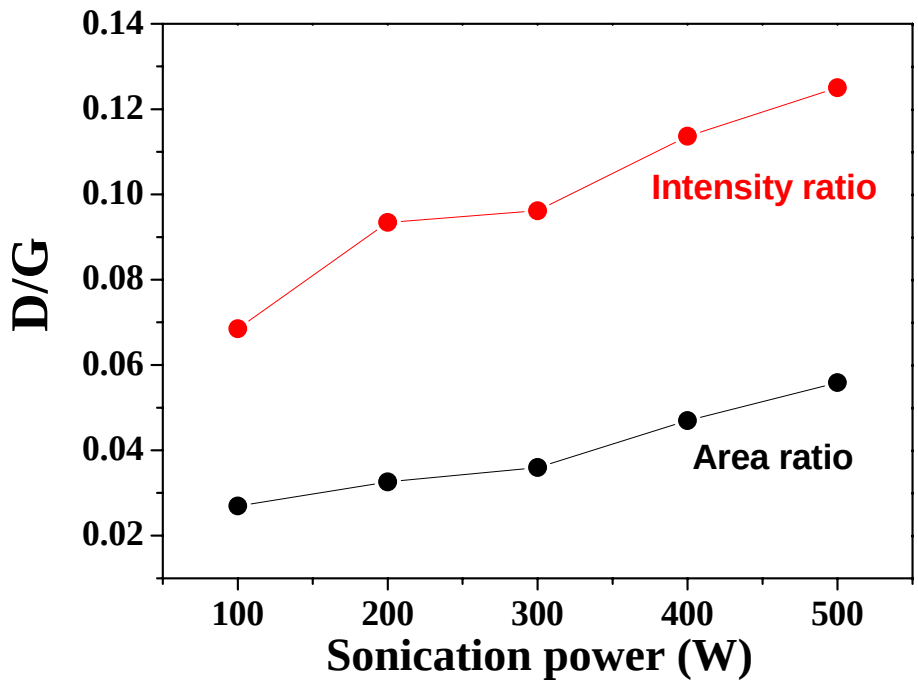
Raman spectra at 633 nm

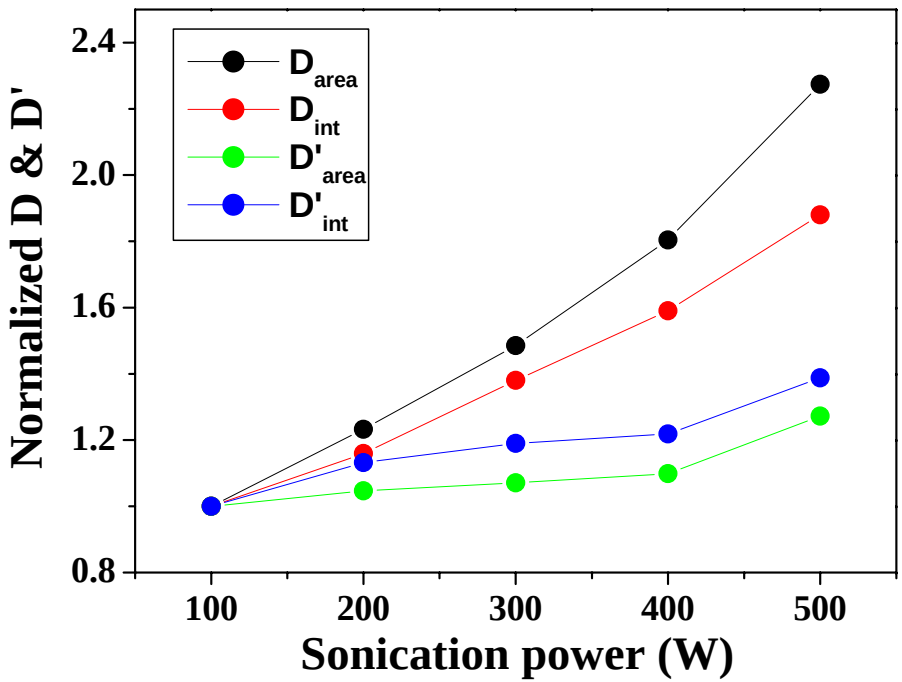


Raman spectra at 633 nm: sonication power



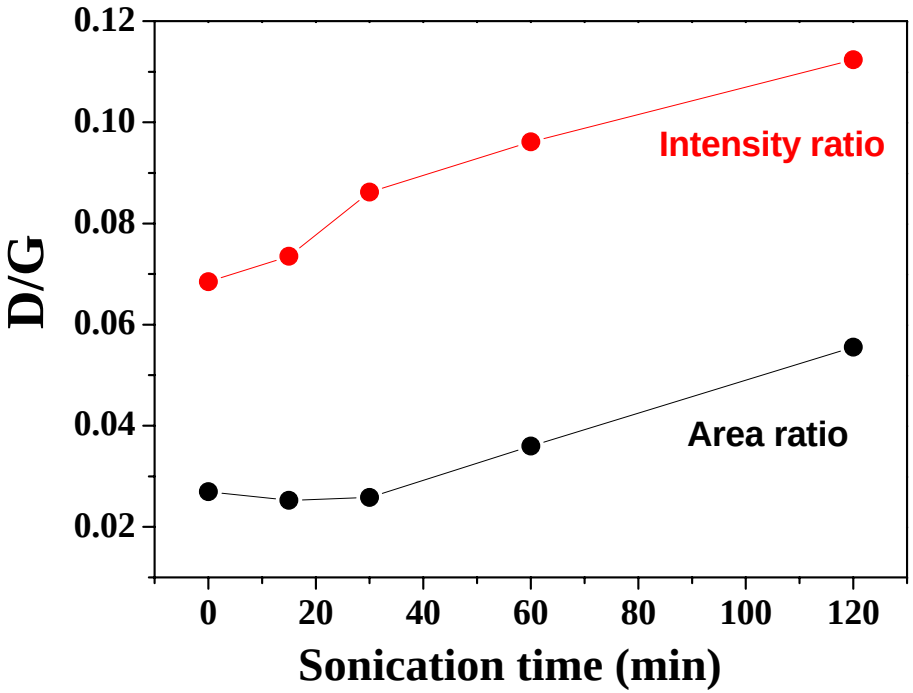
D-band dependence on sonication power (633nm)

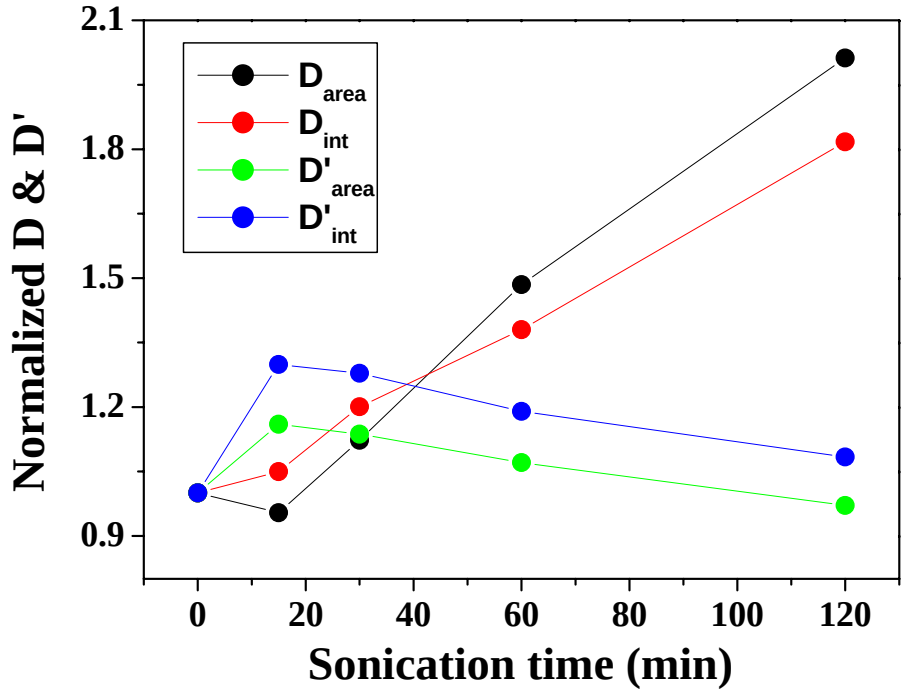




- At 633 nm, both D and D' bands in D/G and normalized one increases with increasing sonication power, in contrast with those at 514 nm.

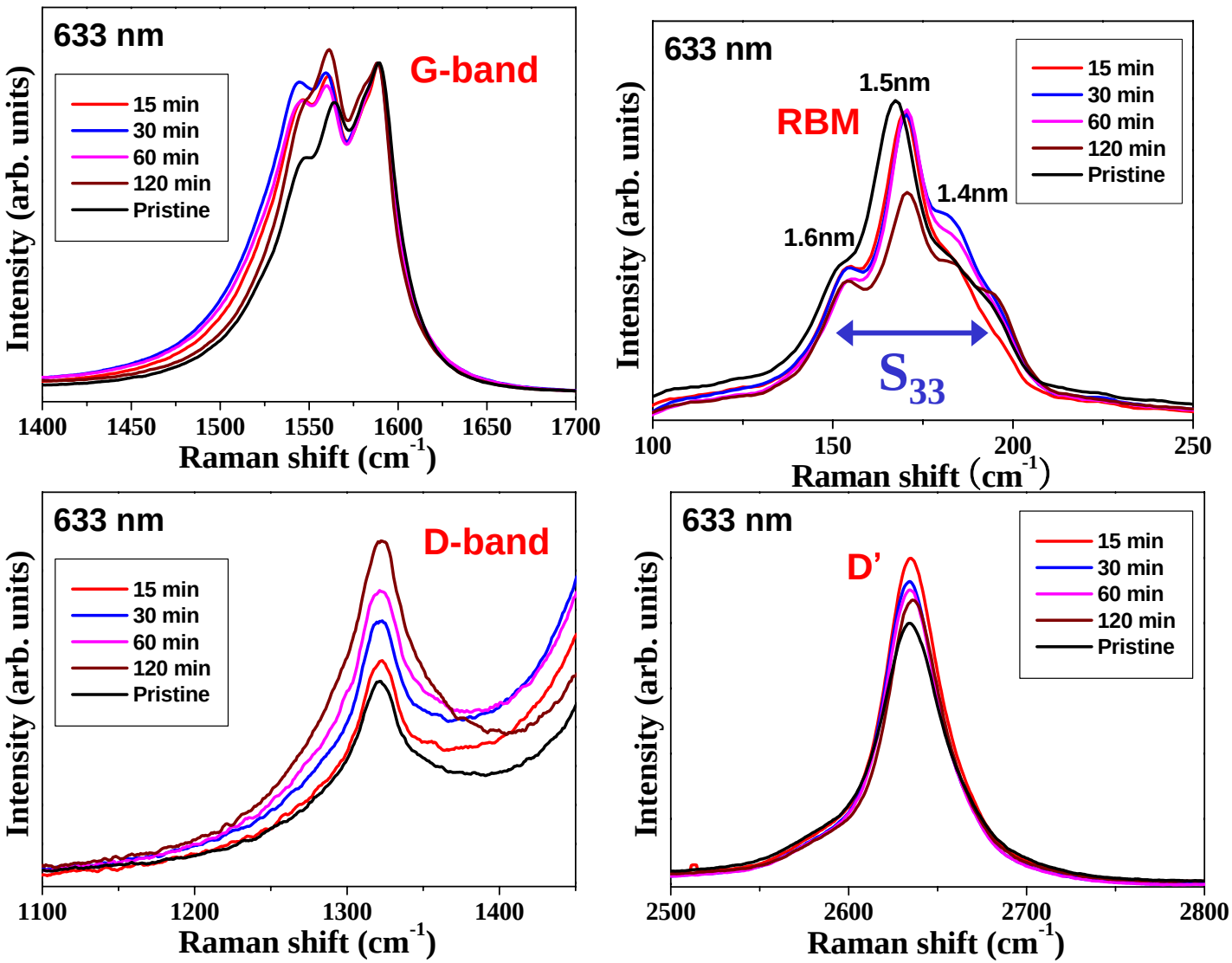
D-band dependence on sonication time at 633 nm



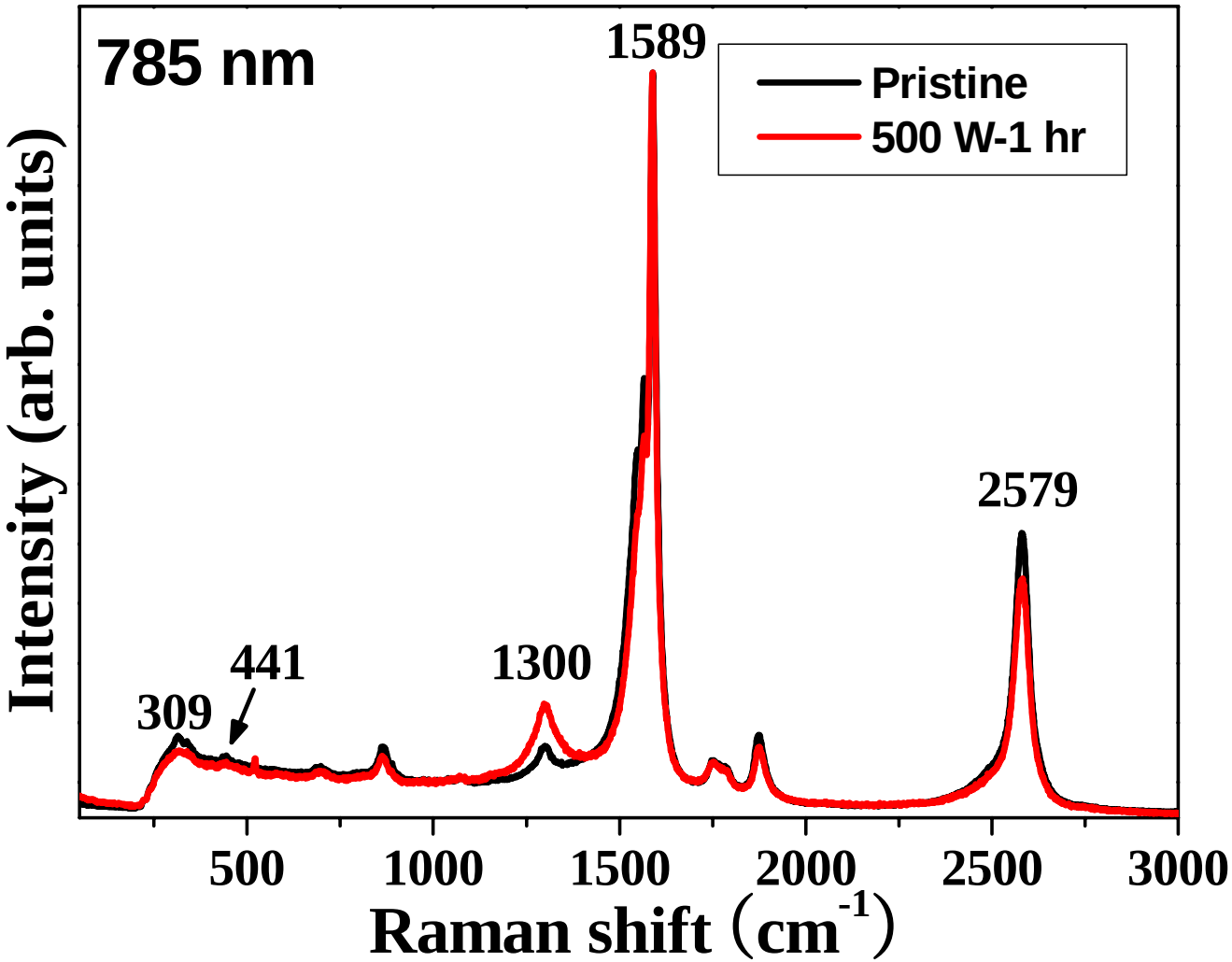


- At 633 nm, D in D/G and normalized one increases the defect formation with increasing sonication power, in contrast with sonication power.

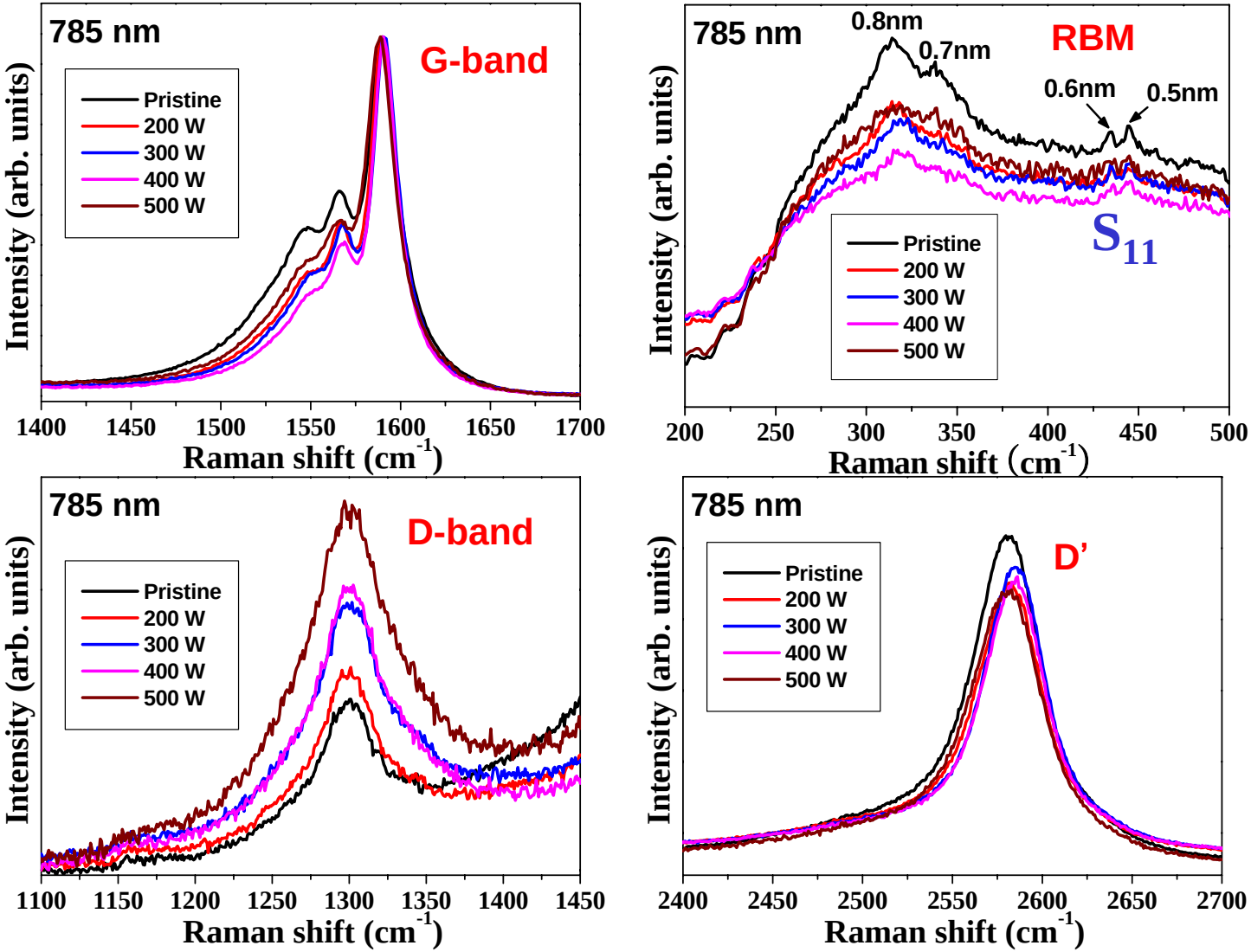
Raman spectra at 633 nm: sonication time at 300 W



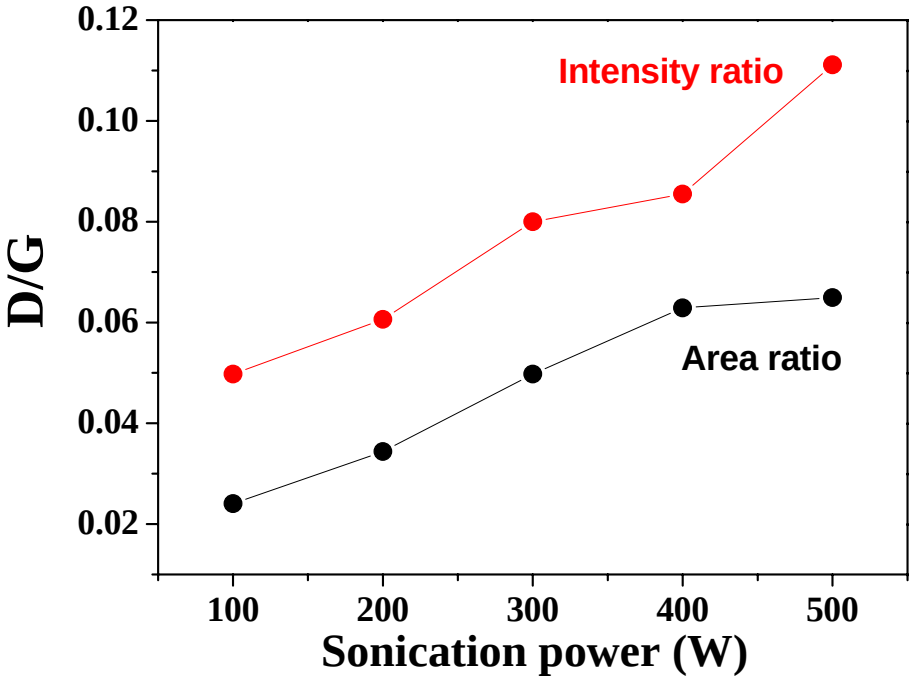
Raman spectra at 785 nm

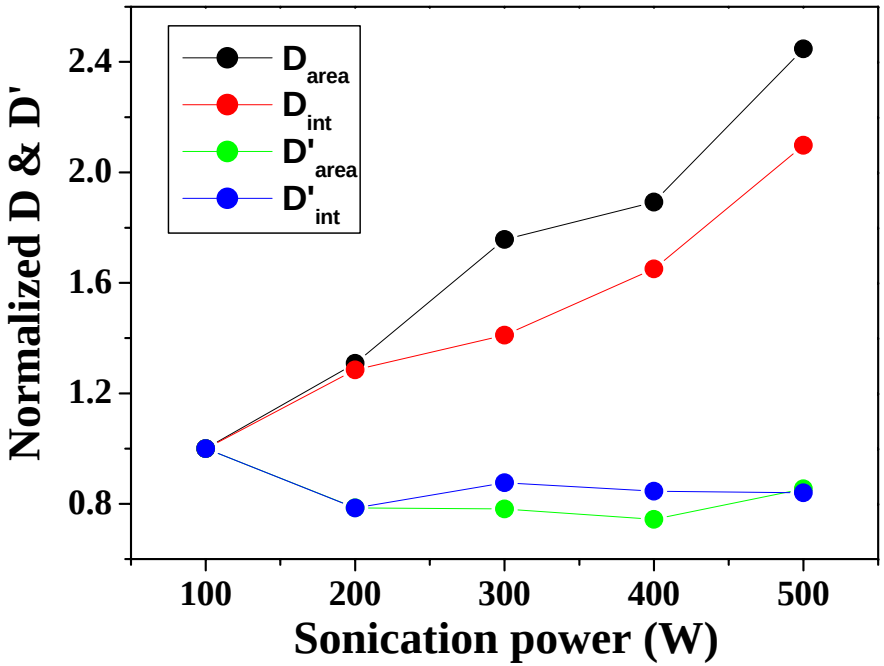


Raman spectra at 785 nm as a function of sonication power in arc-SWCNTs

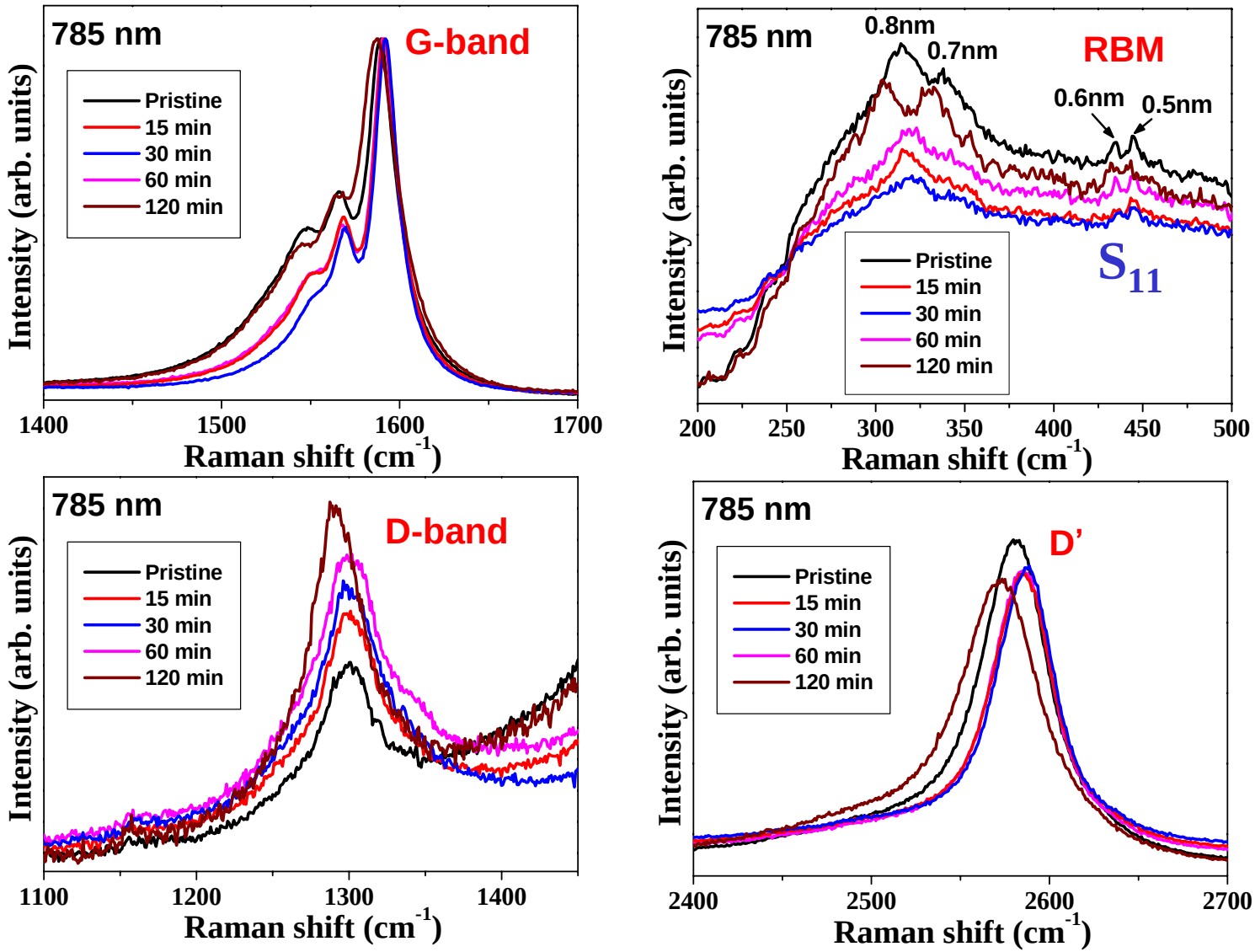


Analysis of Raman spectra at 785 nm as a function of sonication power

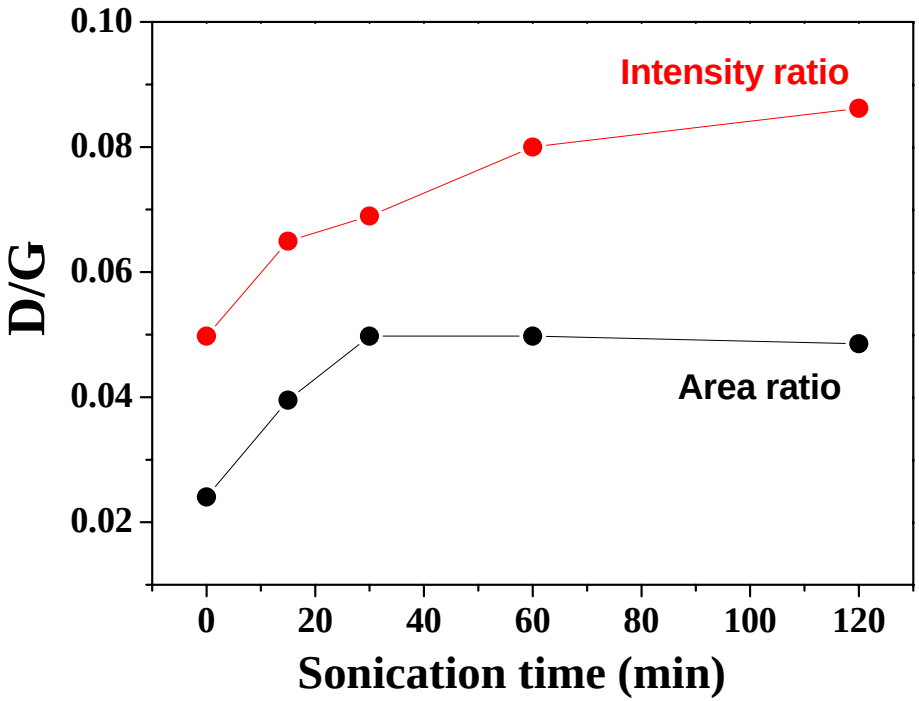


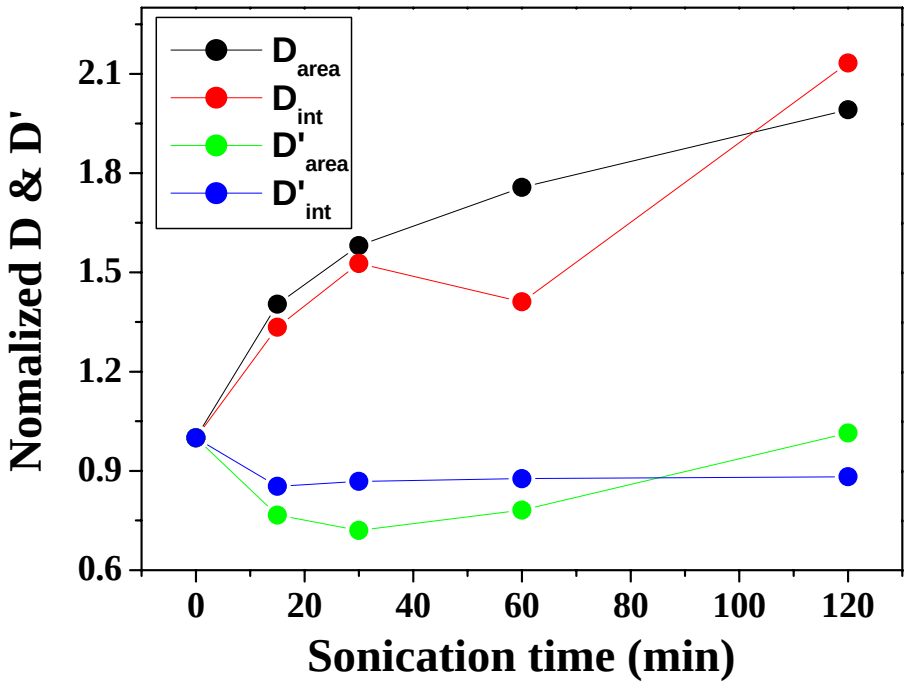


Raman spectra at 785 nm as a function of sonication time at 300 W in arc-SWCNTs

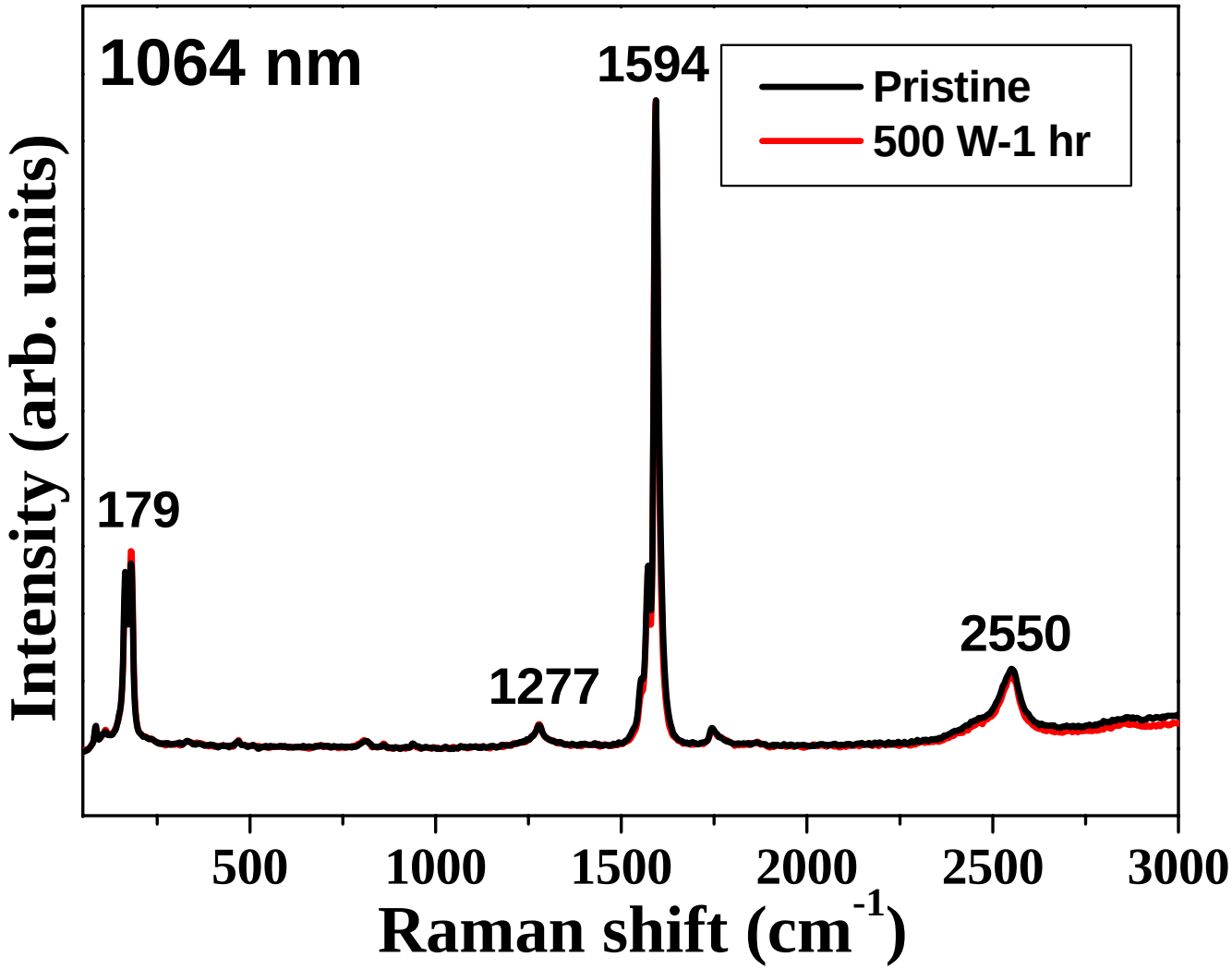


Analysis of Raman spectra at 785 nm as a function of sonication time at 300 W

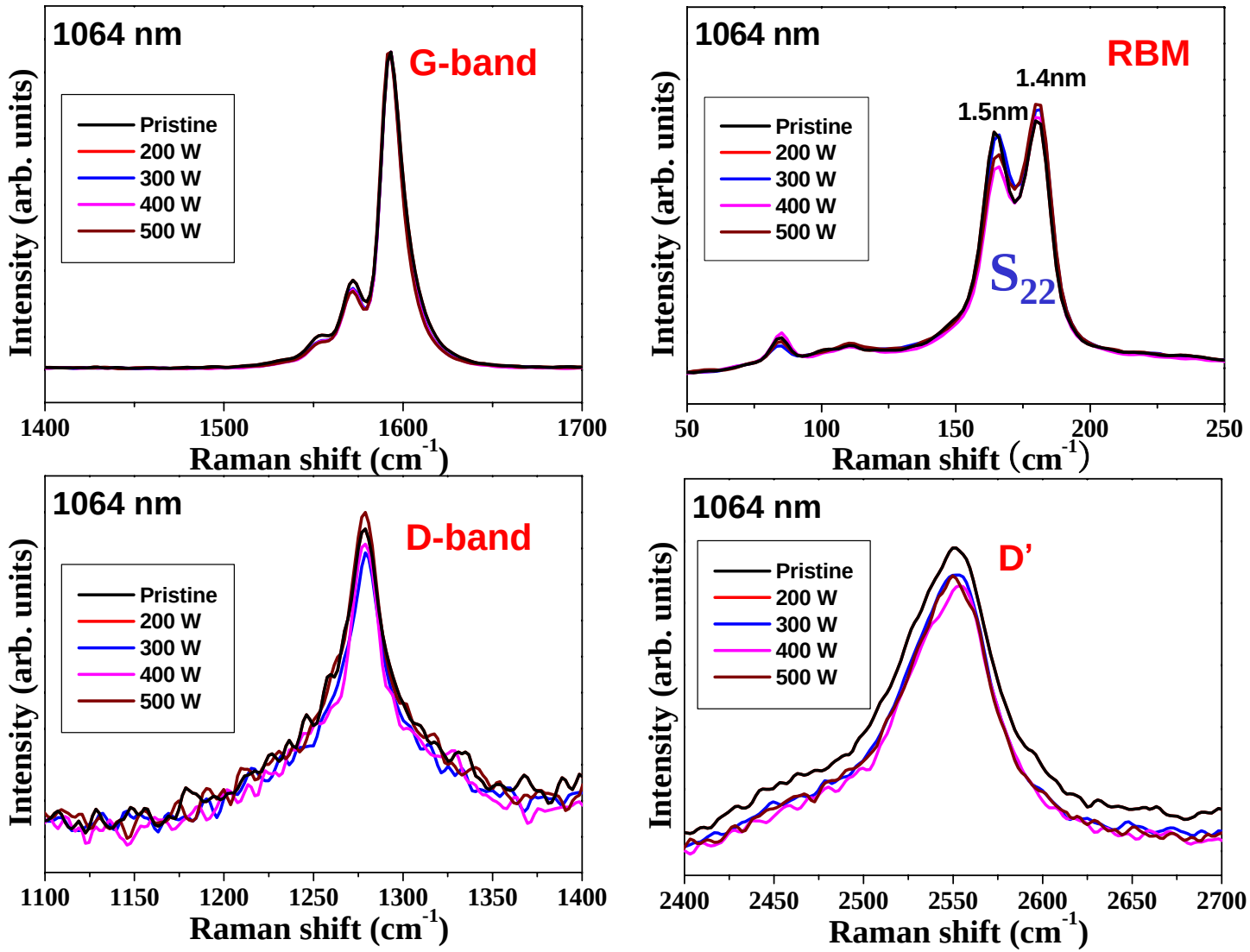




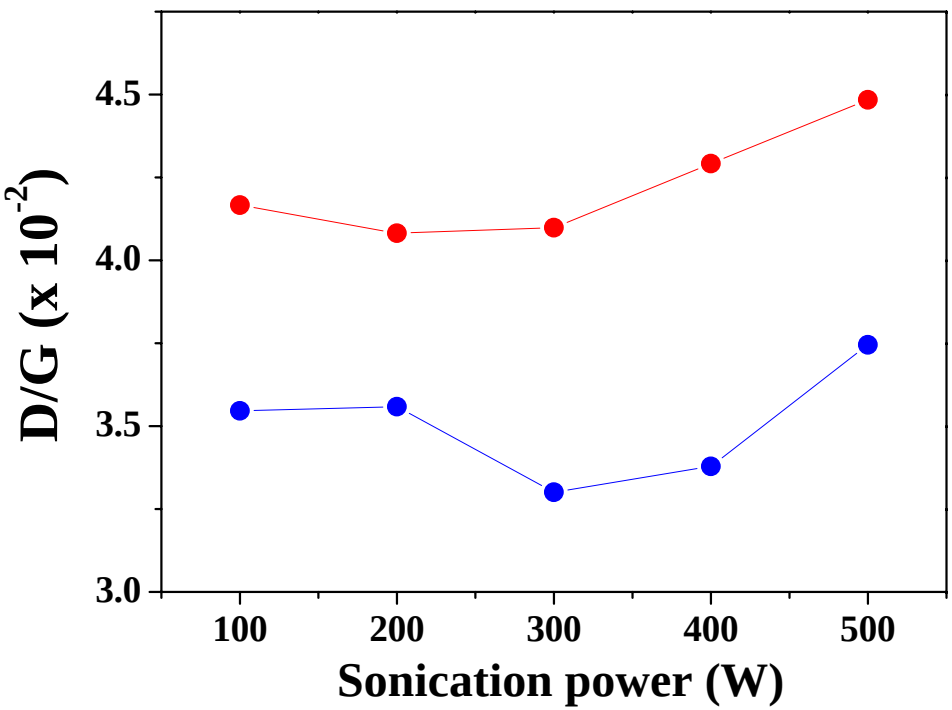
Raman spectra at 1064nm

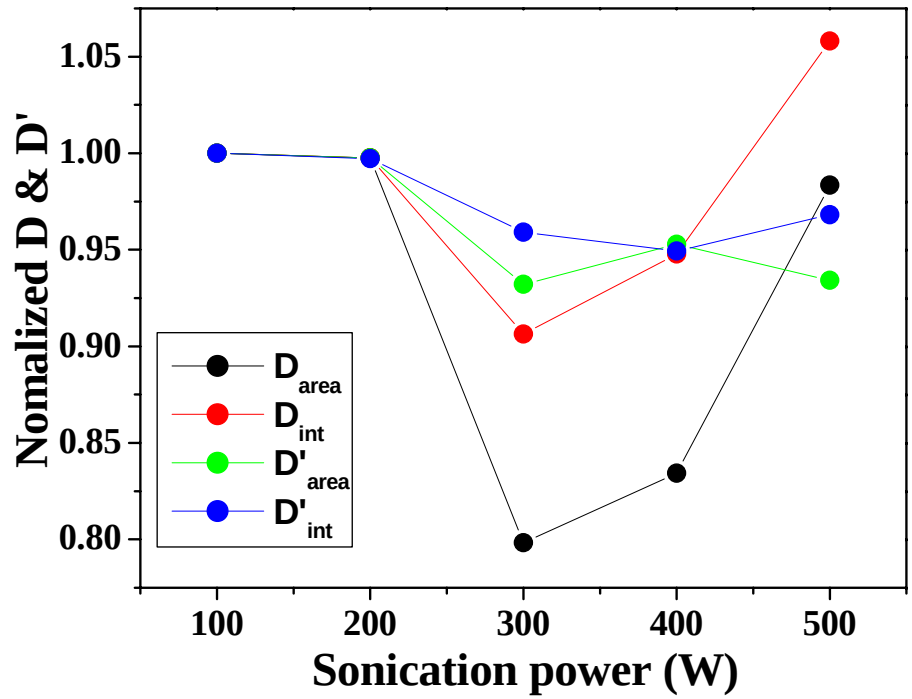


Raman spectra at 1064 nm as a function of sonication power in arc-SWCNTs



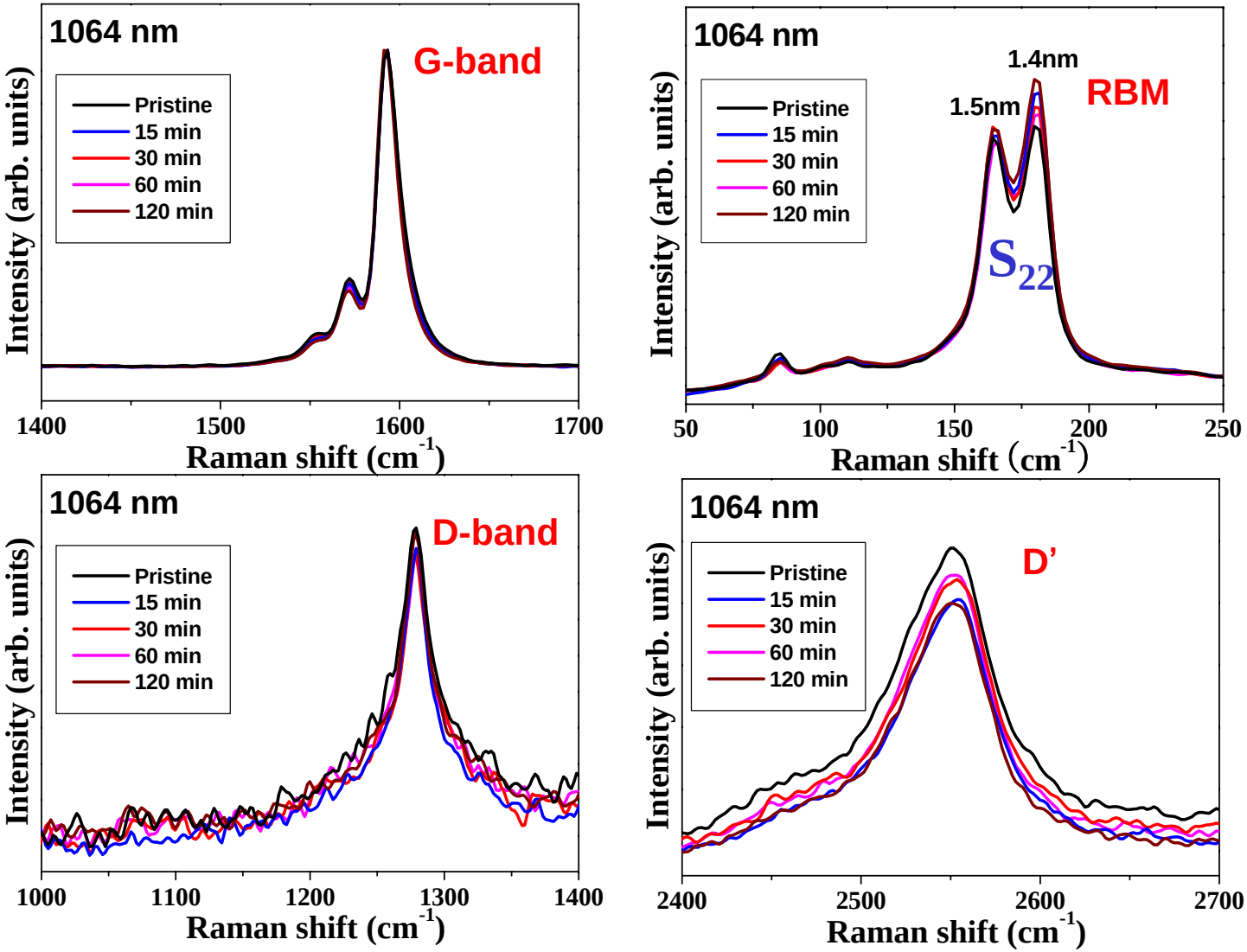
Analysis of Raman spectra at 1064 nm as a function of sonication power



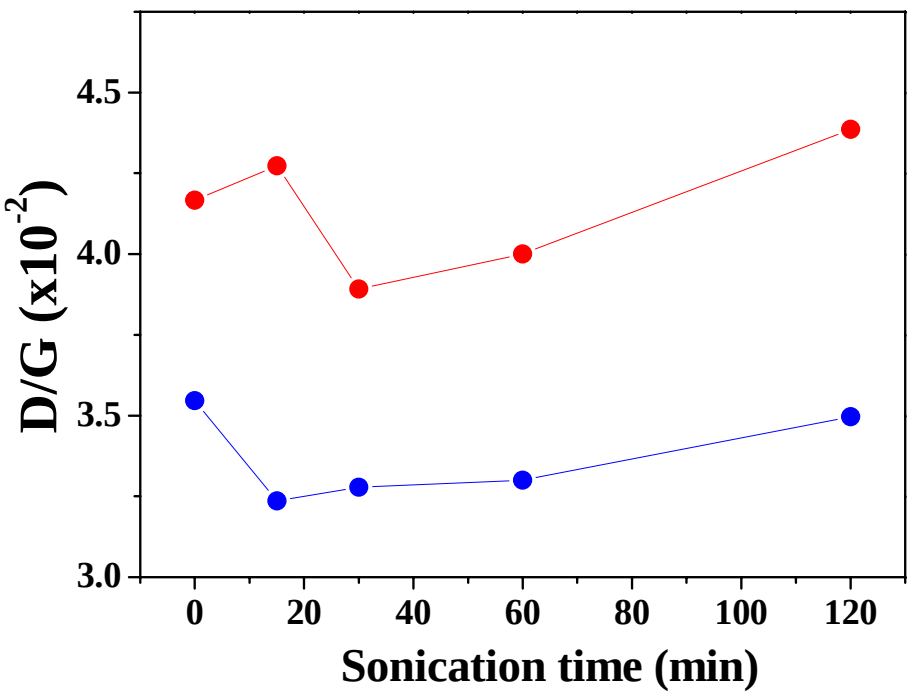


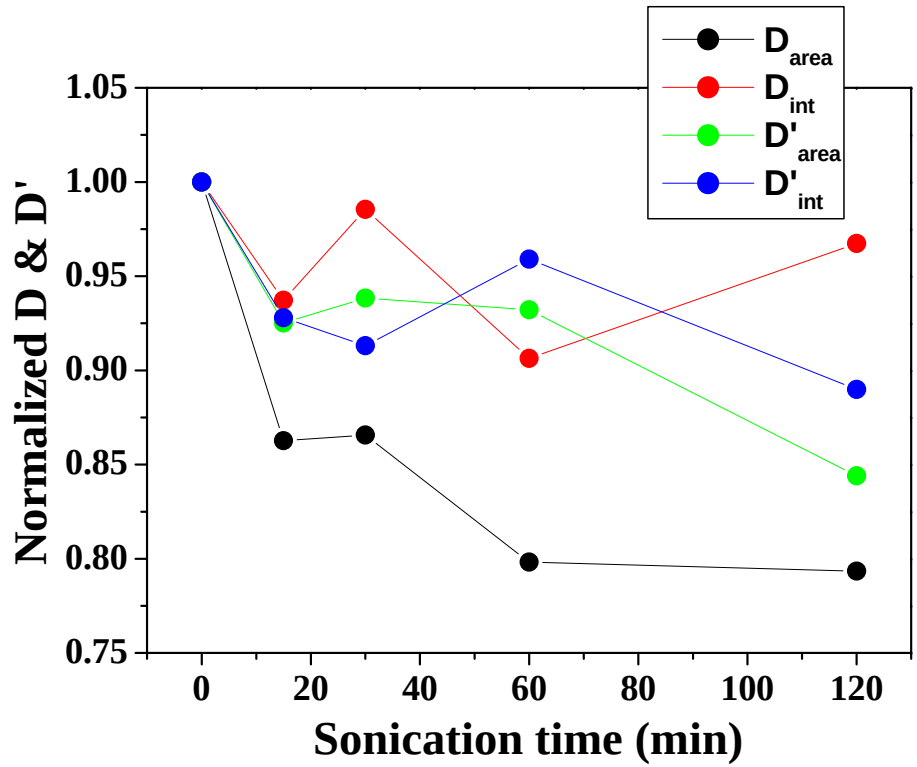
No consistent correlation of D/G with the normalized D and D' band.

Raman spectra at 1064 nm as a function of sonication time at 300 W in arc-SWCNTs



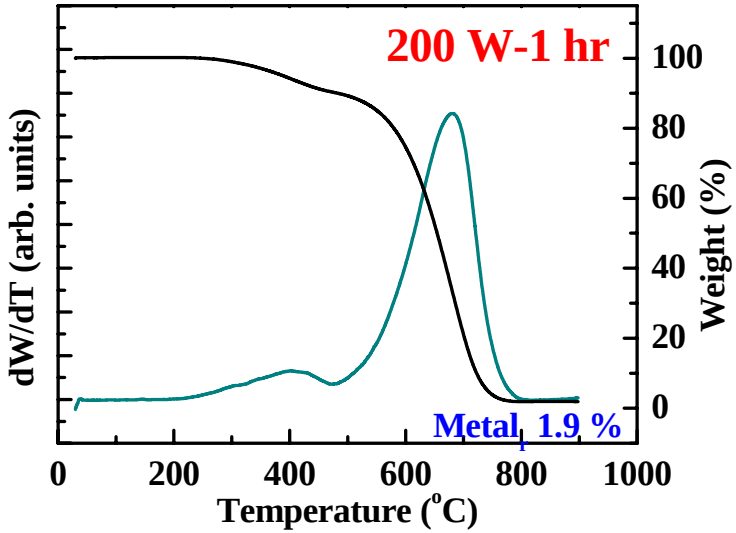
Analysis of Raman spectra at 1064 nm as a function of sonication time at 300 W

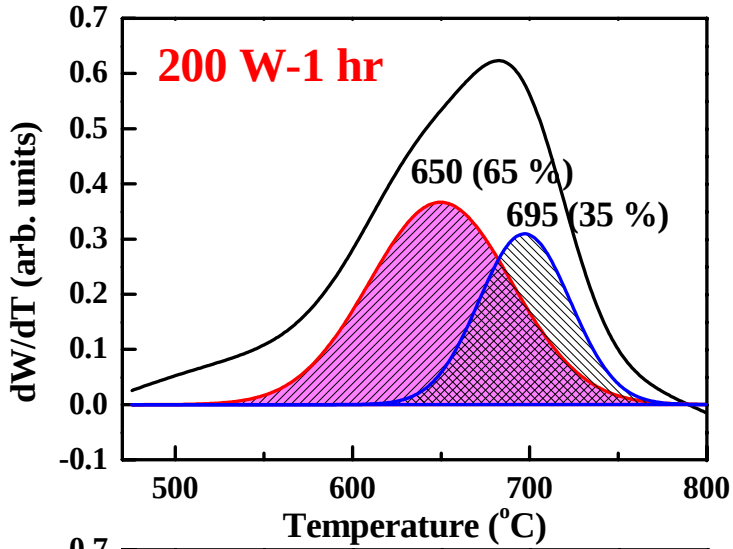


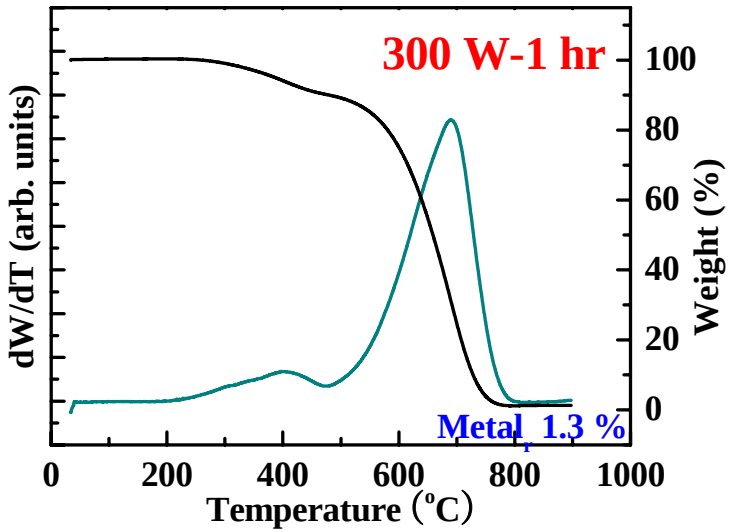


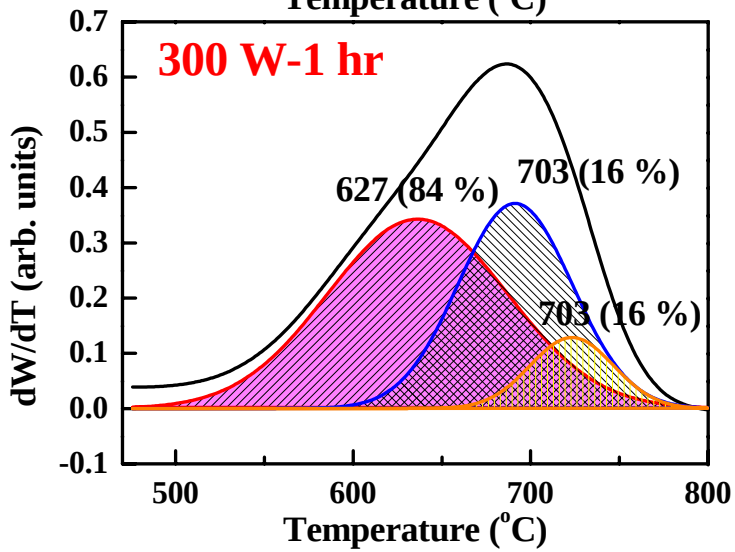
No consistent correlation of D/G with the normalized D and D' band.

Analysis of TGA profile of sonicated SWCNTs synthesized arc-discharge

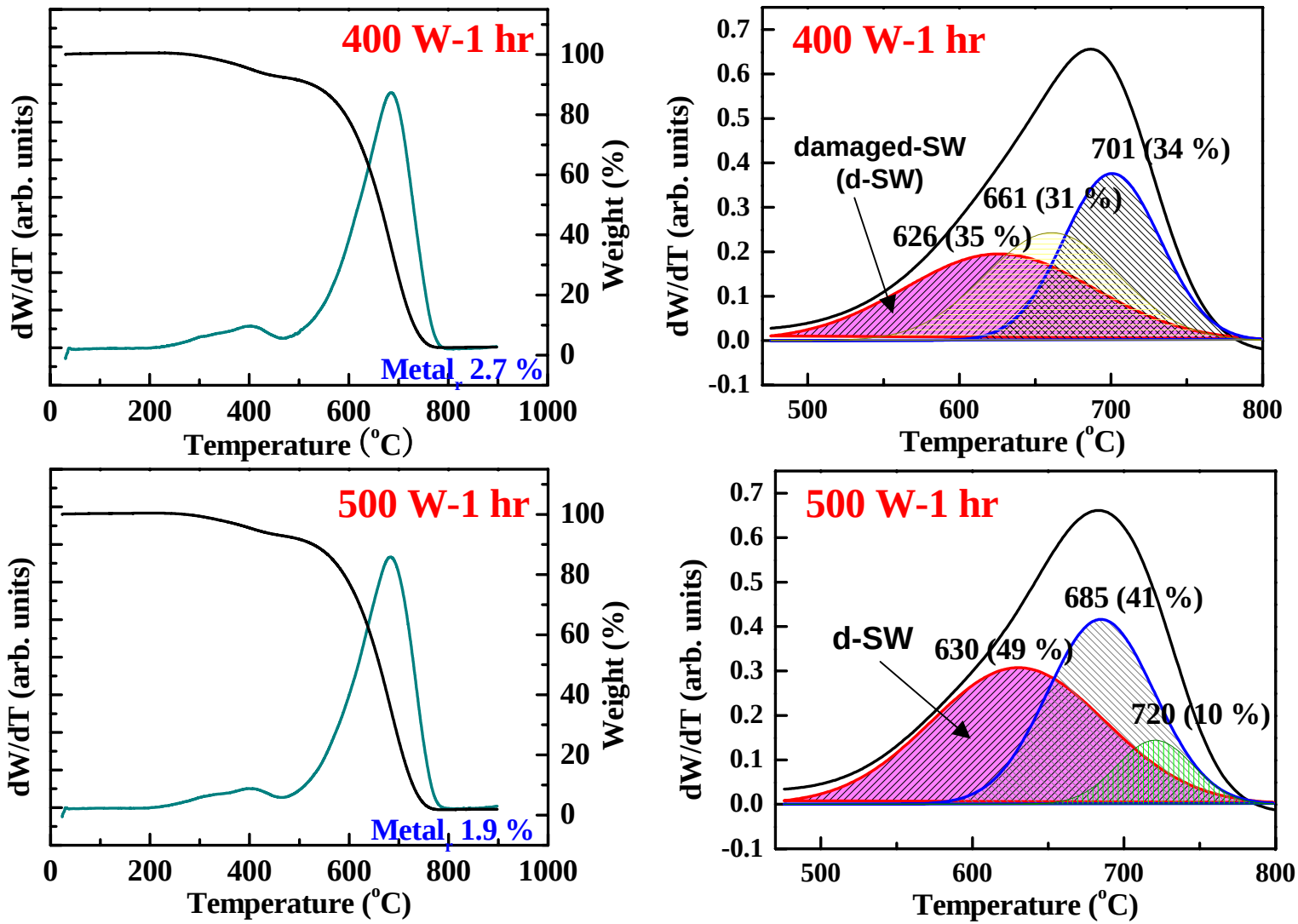




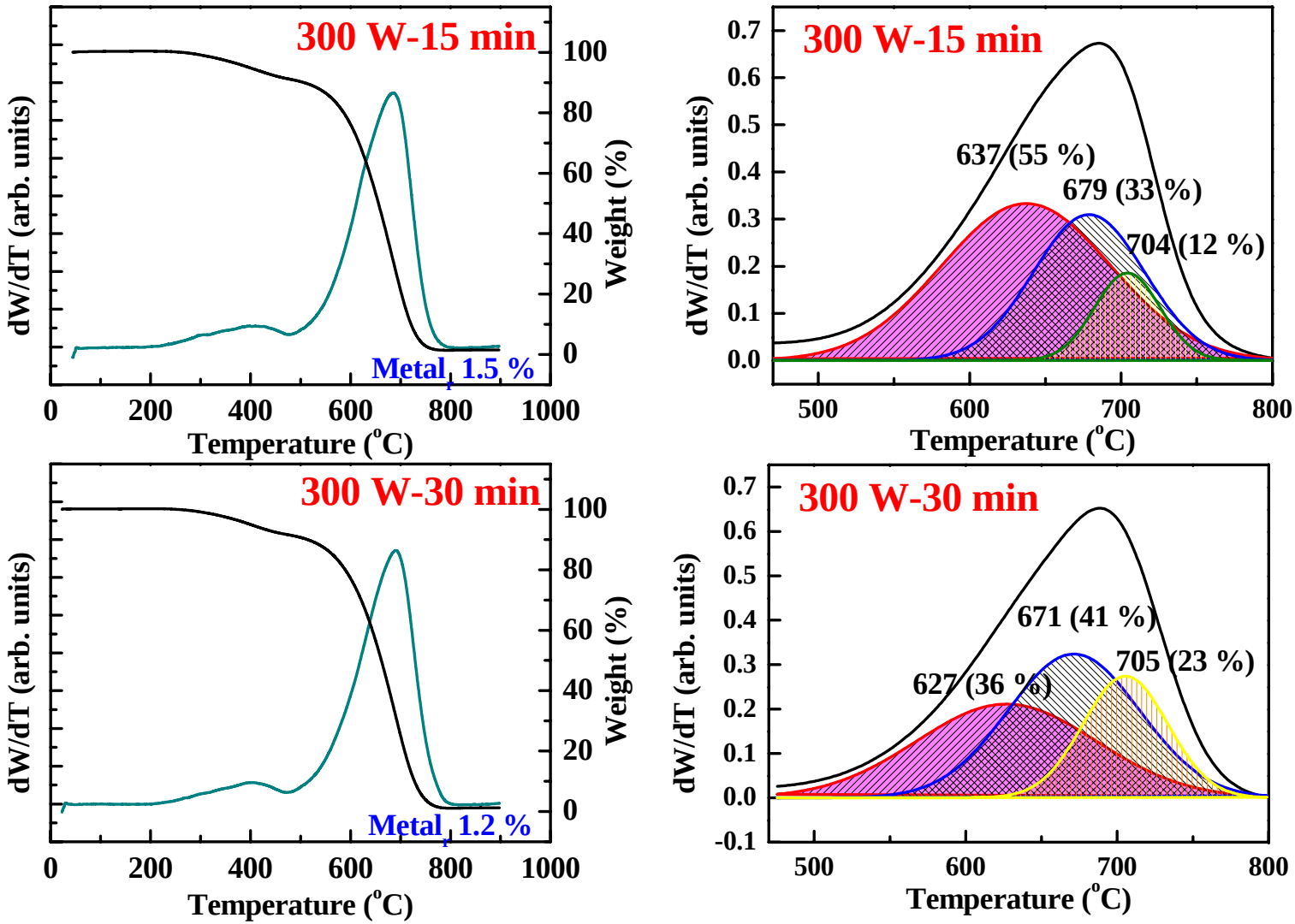




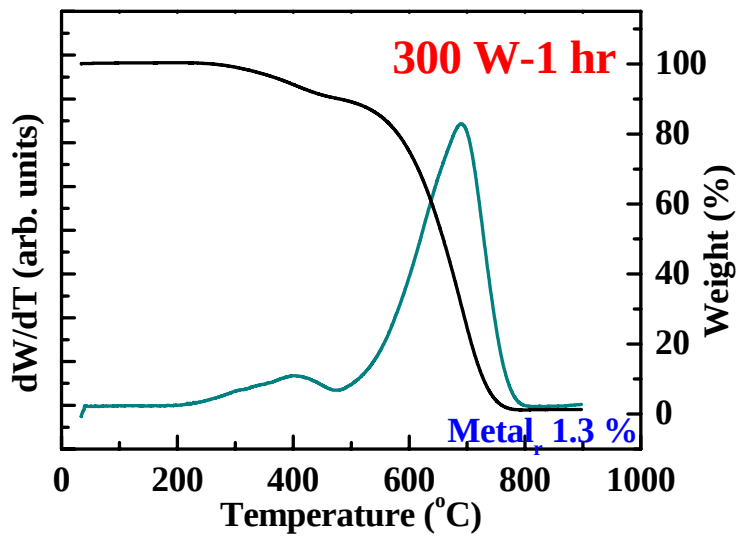
Analysis of TGA profile of sonicated SWCNT synthesized arc-discharge

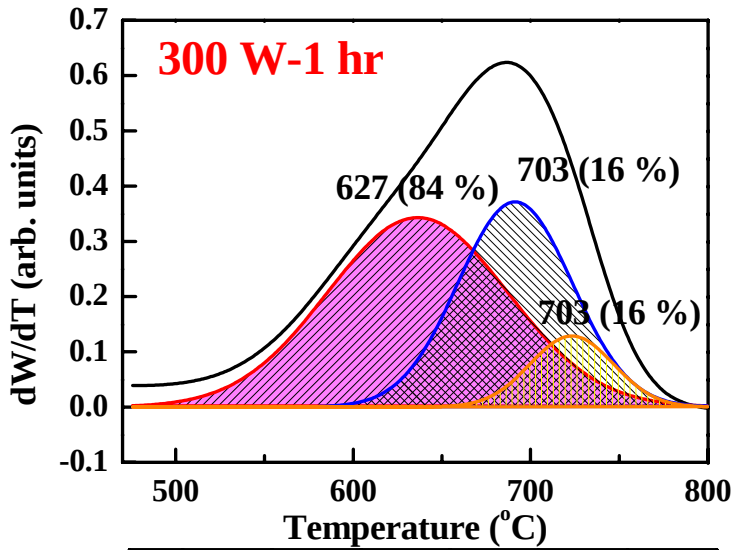


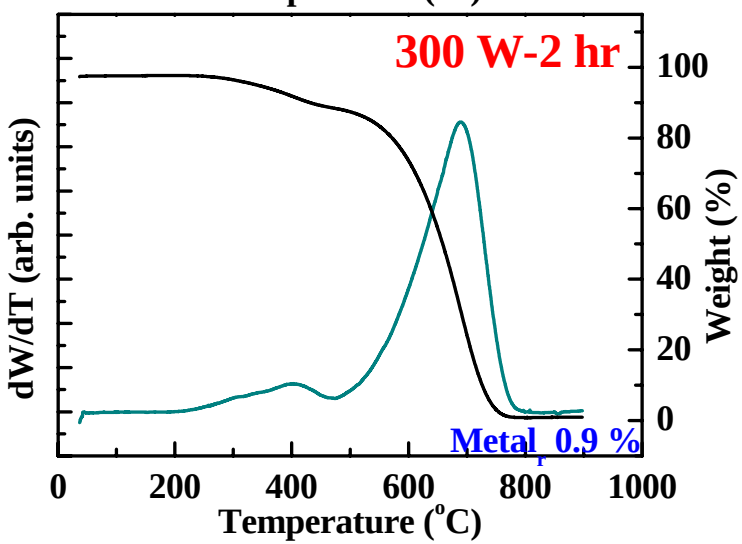
Analysis of TGA profile of sonicated SWCNT synthesized arc-discharge

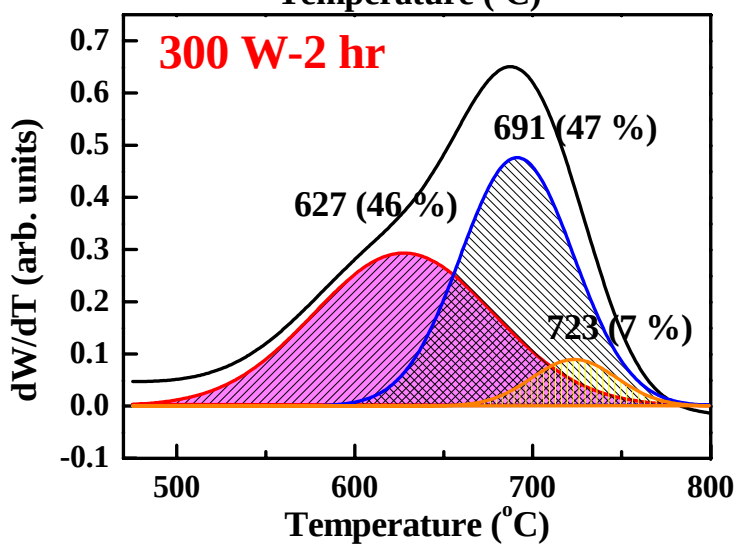


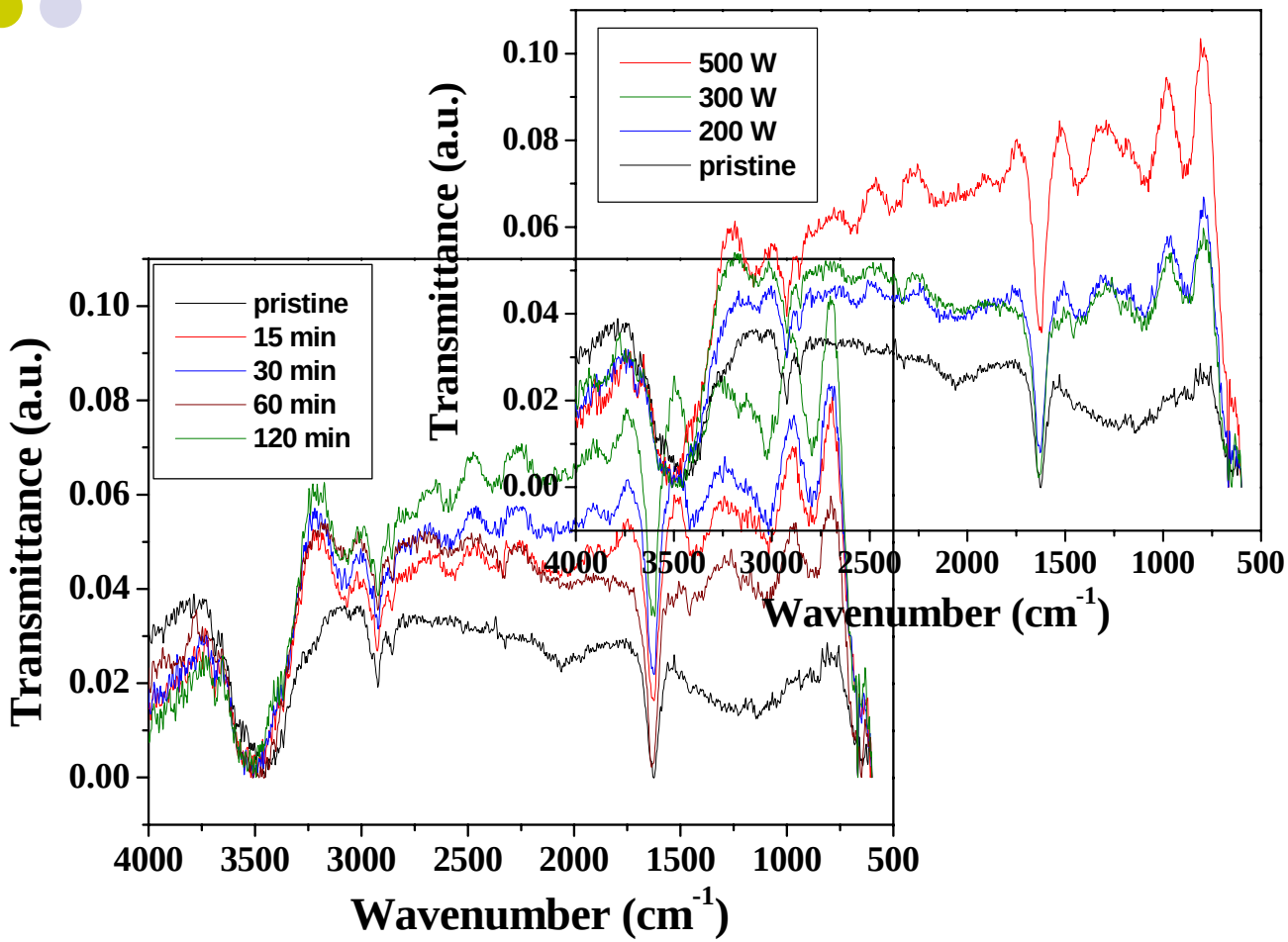
Analysis of TGA profile of sonicated SWCNT synthesized arc-discharge










Transmittance (a.u.)
Wavenumber (cm-1)
pristine
15 min
30 min
60 min
120 min
500 W
300 W
200 W
pristine
0.00
0.02
0.04
0.06
0.08
0.10
4000
3500
3000
2500
2000
1500
1000
500