

***Report on visit to CSIRO Austrasia  
-Long-term placement program-***

Placement : CSIRO Sydney Austrarilia

Period : 27<sup>th</sup> January to 28<sup>th</sup> March for 2 months

Presenter : Hitoshi Watanabe Nagoya Univ.

# *Outline*

- ✓ Location
- ✓ Photo of lab. and researchers
- ✓ What is CSIRO
- ✓ The purpose of this visiting
- ✓ Presentation and Guidance
- ✓ After presentation
- ✓ Collaboration with CSIRO in the paper
- ✓ What have I learned through ITP?

# Location

Location of laboratory: Sydney Australia



## From Japan to Australia

- Airplane: 11 hours

## From inn to CSIRO

- Bus and train : 1 hours

## Sydney

- ✓ Opera house
- ✓ Olympic (2000)
- ✓ the biggest population city in Australia
- ✓ Sightseeing

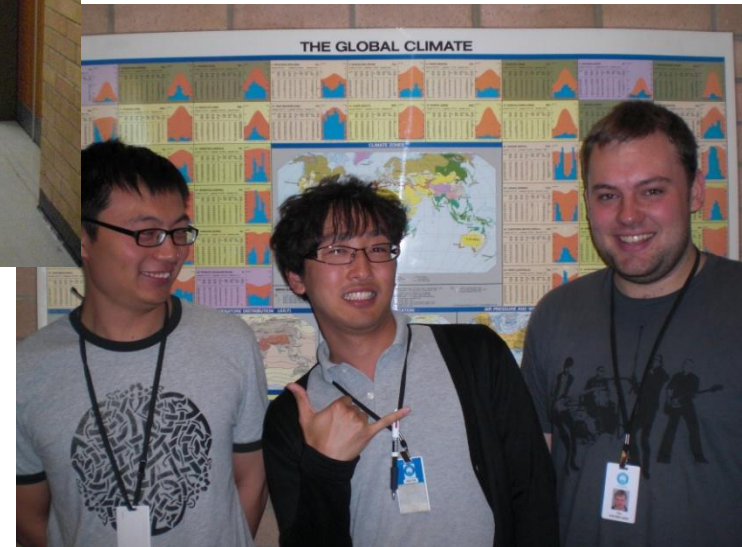
## Weather and temperature

- ✓ Mostly fine day
- ✓ Not humid
- ✓ Summer season
- ✓ Strong light of the sun





# *Photo of lab. and researchers*





# What is CSIRO?

Commonwealth Scientific and Industrial Research Organization : CSIRO

URL: <http://www.csiro.au/>

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Information, analysis and commentary from the university and research sector.

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National Challenges [National Research Flagships](#) [Flagship Collaboration Fund](#)

Seeing through cells eyes

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This research group: Australian government

Found year: 1916

Main office: Canberra

Branches: 60 (including overseas)

Number of staff: more than 6,500 people

Research filed: Extremely wide

# *This purpose of ITP this time*

Branches: 60 branches (including overseas)  
Number of staff: more than 6,500 people  
Research filed: extremely wide

They have .....

“**knowledge, own experience and technical know-how**”.

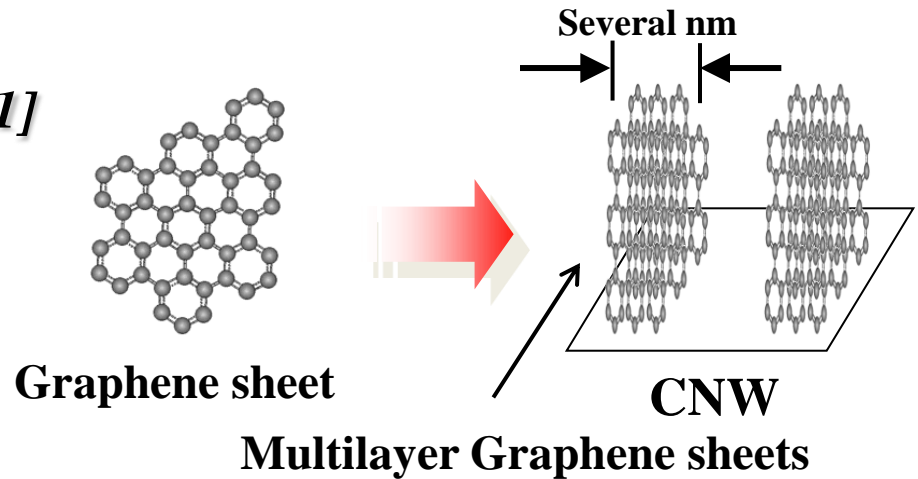
## Purpose

To discuss the mechanisms of hydrophobic and hydrophilic surface properties of CNWs, next paper and PhD candidate plan.

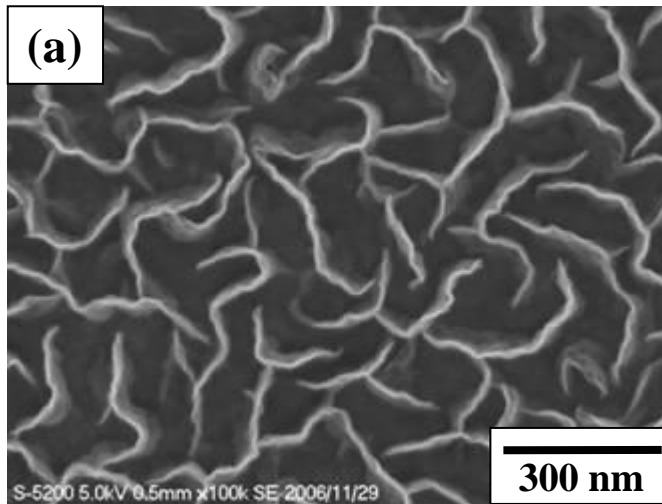
# *Presentation for ITP period*

## *CNW : Carbon nanowall<sup>[1]</sup>*

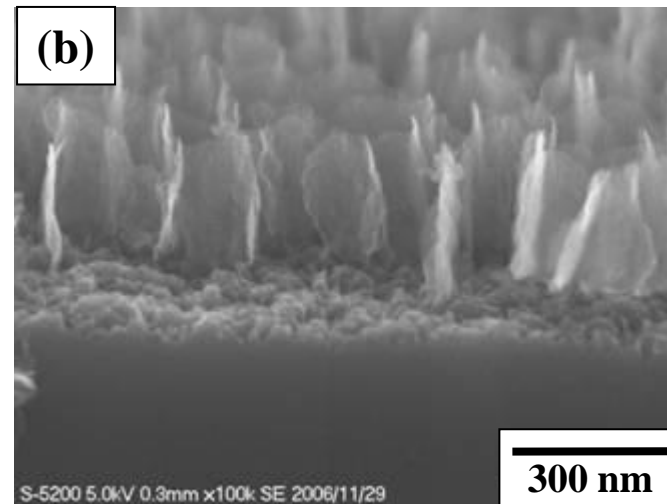
The CNW, consists of multiayer graphene sheets, stands vertically on substrate.



## The SEM images of CNW



(a) The SEM image of CNW

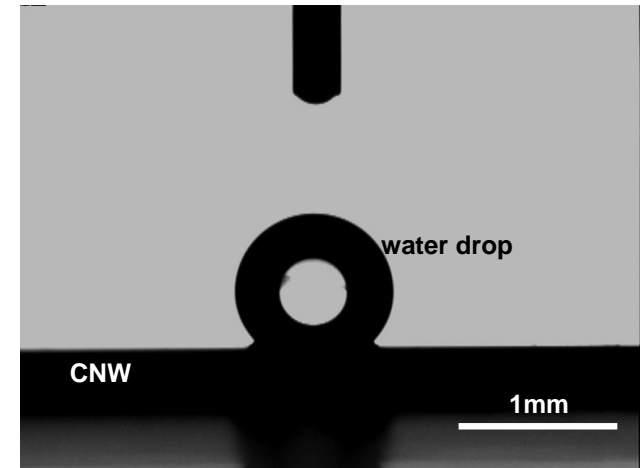


(b) The birds-eyes view of CNW

[1] M. Hiramatsu, K. Shiji, H. Amano, M. Hori, Appl. Phys. Lett. 84 (2004) 4708.

# *Purpose of this study*

- ◆ CNWs intrinsically have hydrophobic properties due to
  - High aspect ratio
  - Maze-morphology
  - Incorporated fluorine atoms



✓ For biosensing applications of CNWs, it is important to control the contact area of CNWs to reagent solutions including DNA, cancer and protein.

➤ Development and control of hydrophilicity are indispensable.

## Purpose

To clarify mechanisms of hydrophobic and hydrophilic surface properties of CNWs and establish their control techniques.



# *Experimental set up*

## ■ Procedures

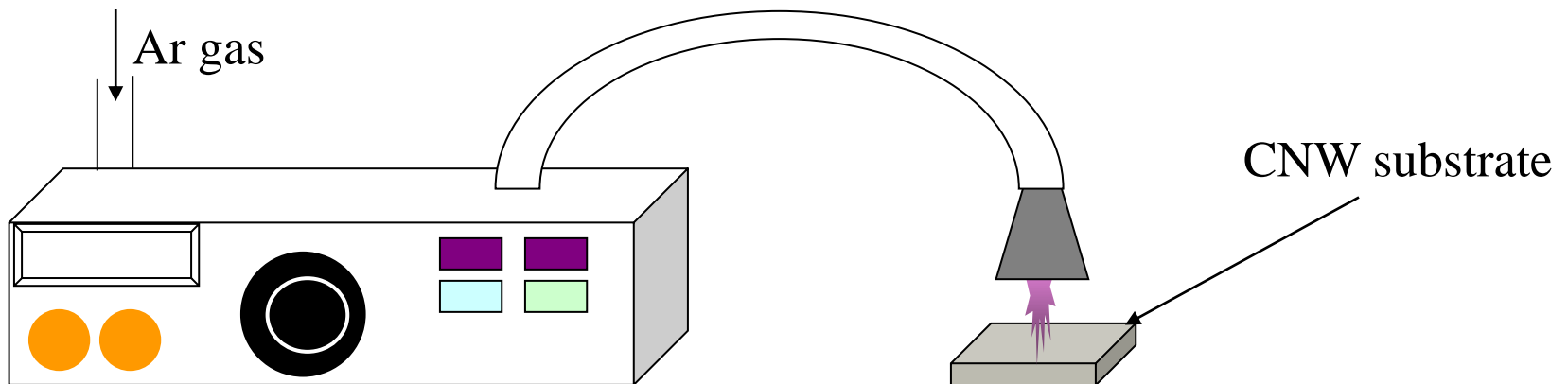
- ① Growth of CNWs by Radical Injection Chemical Vapor Deposition.
- ② Surface treatment by atmospheric pressure plasma using Ar gas.
- ③ Evaluation of contact angle and chemical bonding states.
  - Drop shape analysis (DSA)
  - X-ray photoelectron spectroscopy (XPS)

## ■ Set up

Gas: Ar, Flow rate: 2 l/min, Applied voltage: 60 kV

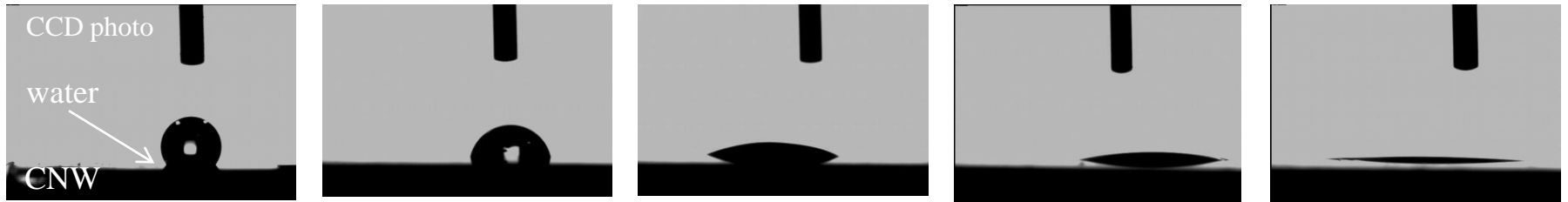
Distance between substrate and plasma source: 5 mm

Plasma treatment times: 0, 1, 5, 15, 30s



# CNW with/ W.O. plasma surface treatment

CNW fabricated from  $C_2F_6$



Plasma surface treatment time

0 times

1 times

5 times

15 times

30 times

Contact angle

$137.3^\circ$

$88.1^\circ$

$26.8^\circ$

$13.7^\circ$

$6.2^\circ$

CNW fabricated from  $CH_4$



Plasma surface treatment time

0 times

1 times

5 times

15 times

30 times

Contact angle

$133.3^\circ$

$84.4^\circ$

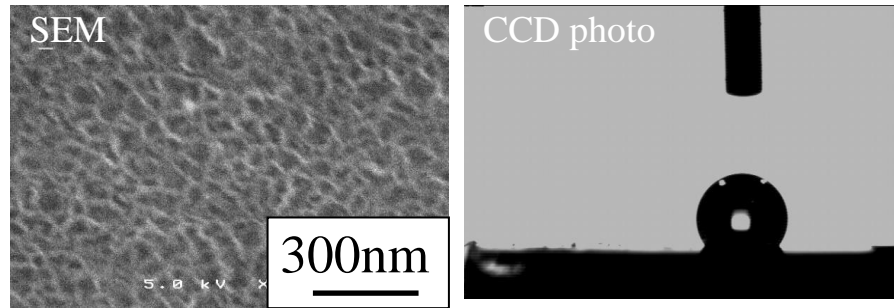
$7.5^\circ$

$4.5^\circ$

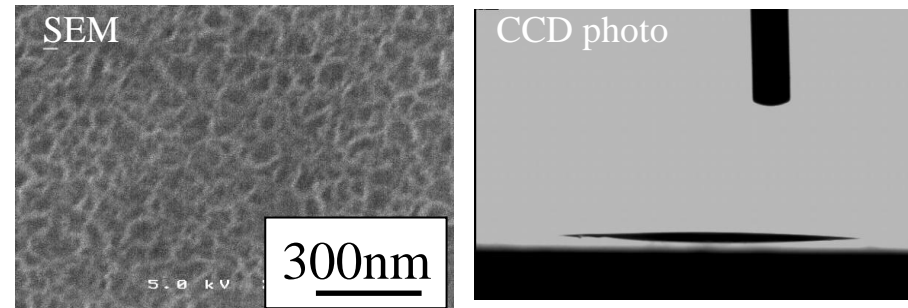
$3.5^\circ$

# Raman spectrum

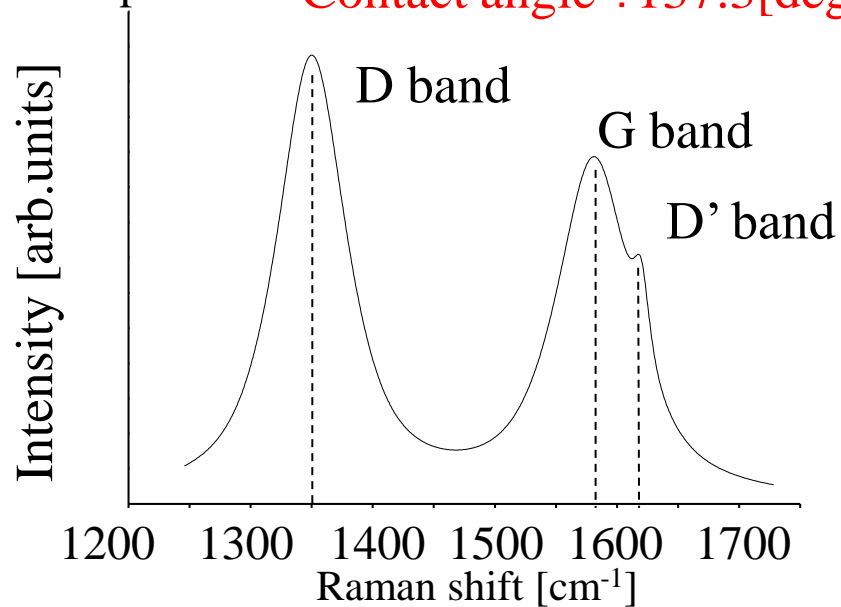
Before



After



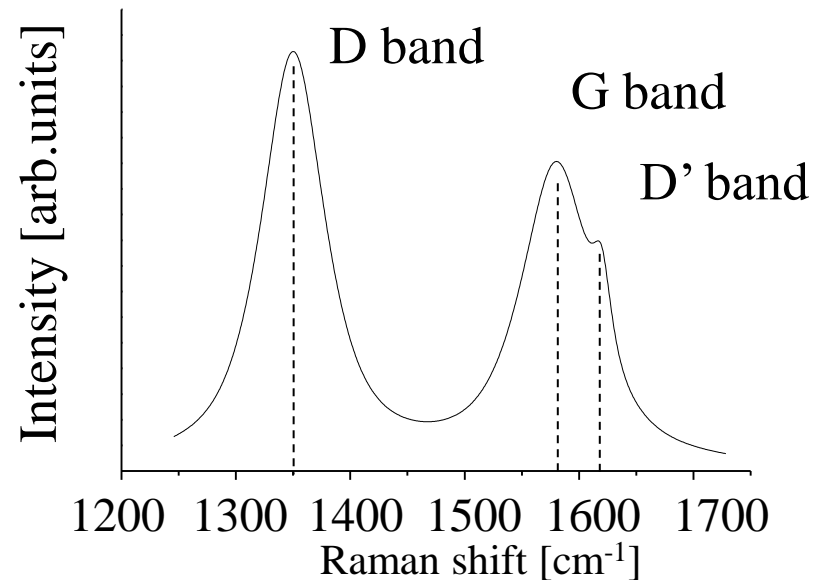
Raman spectrum **Contact angle : 137.3[deg]**



$$I_D/I_G = 1.2$$

- ✓ Drastic change of contact angle by plasma surface treatment
- ✓ No significant change in morphology and crystallinity

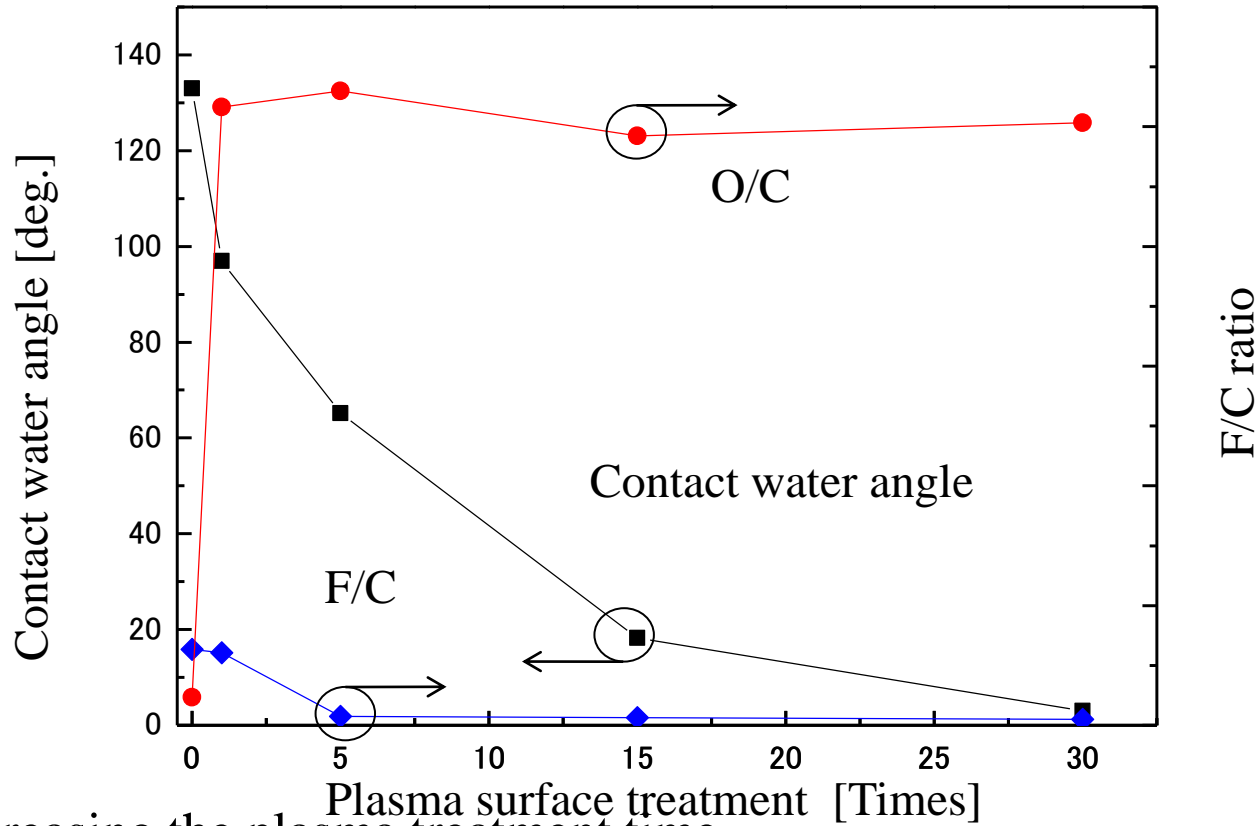
**Contact angle : 6.2[deg]**



$$I_D/I_G = 1.3$$



# XPS of CNW fabricated from $C_2F_6$

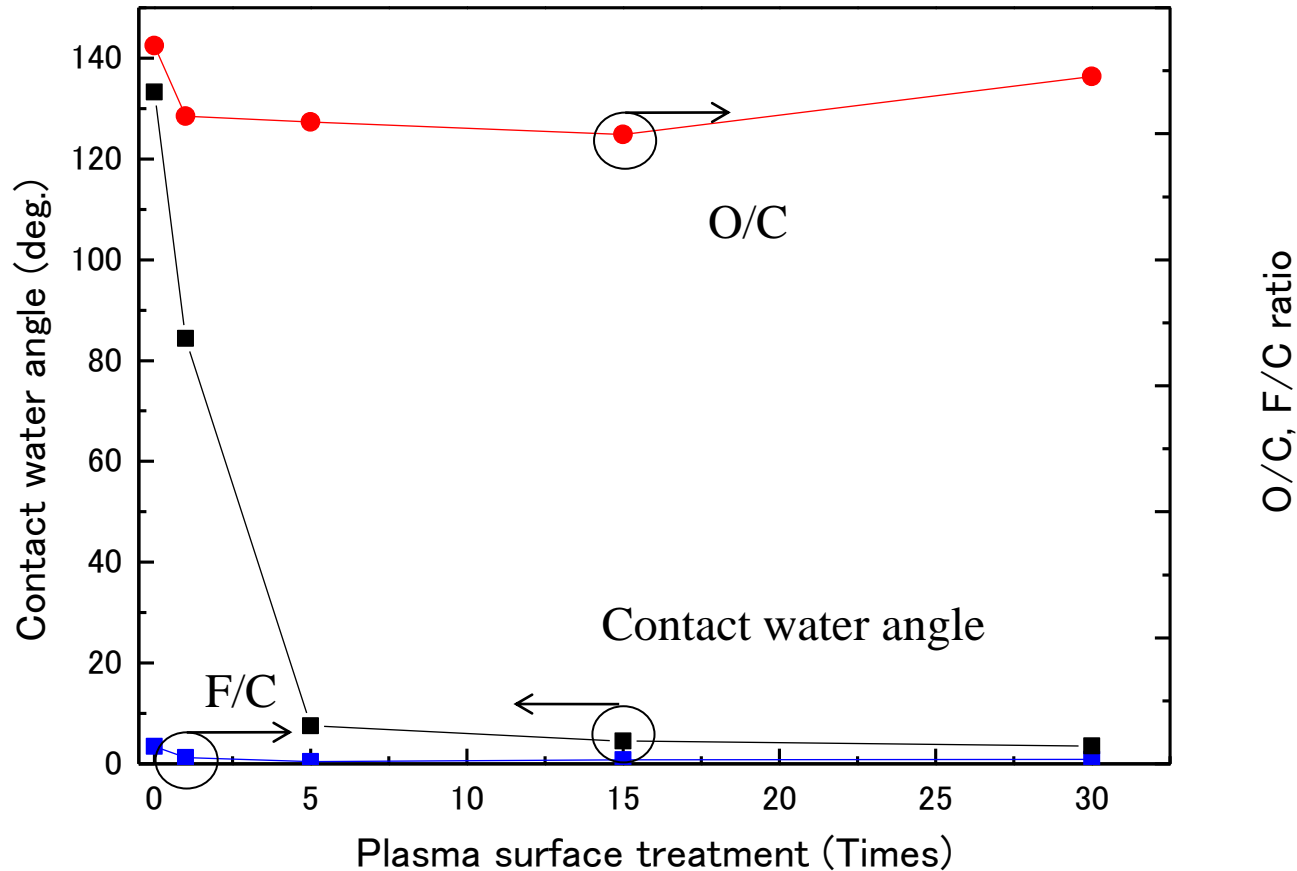


With increasing the plasma treatment time,  
Fluorine (F) / carbon(C) ratio decreases but oxygen(O) / C ratio increases,  
while the contact angle decreases.



Detachment of F atoms and adsorption of O atoms could induce the hydrophilic property of CNW surface.

# XPS of CNW fabricated from $CH_4$



- ✓ O atom is on the surface W.O. plasma surface treatment.
- Because of the layer of natural oxidation
- ✓ Checking the aging effect of hydrophilic property .
- Too high contact water angle W.O. plasma surface treatment

# *After my presentation*

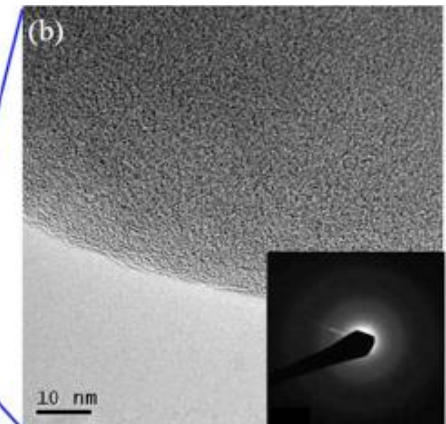
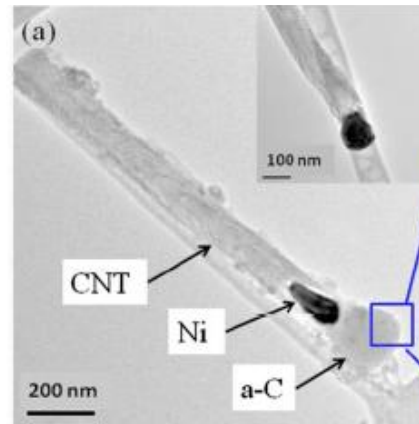
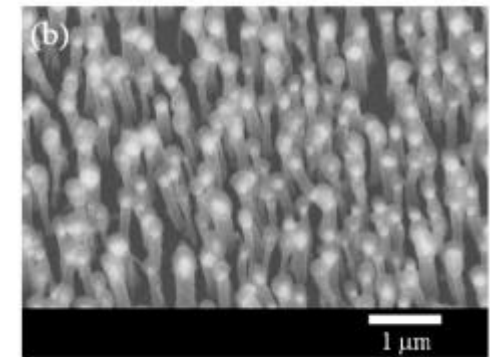
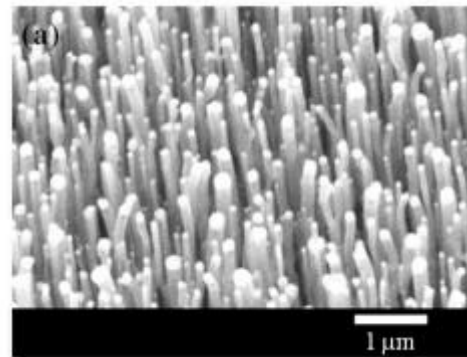
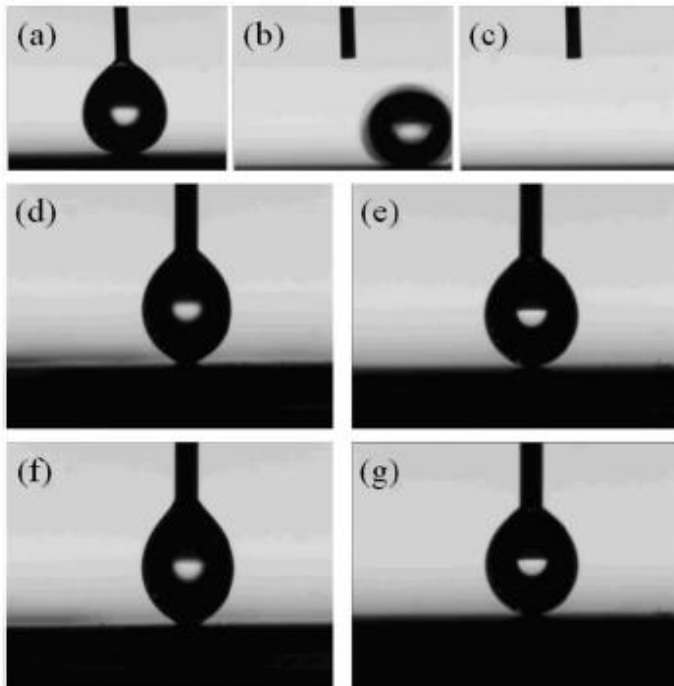
## Some advise

- ✓ Rapid utterance
- ✓ Keep in time
- ✓ Many slide

## They are interested in and discusses....

- ✓ “XPS and contact water angle of CNW fabricated from CH<sub>4</sub>”

Why.....?





# Collaboration with CSIRO in the paper

**Plasma-assisted, controlled wettability properties of self-organised vertically oriented graphene nanosheets (title will be a lot more attractive)**

**Outline:**

(I) Unique and unusual properties of graphene nanosheets (GNSs), significance problem for achieving very thing nanosheets and controlling their properties for their potential applications in nano-electronics, field-electron emission devices, chemo and biosensors.

(II) Justifying the novelty of plasma-based approach for growth of GNSs by using the precursor gases, CH<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> gas and mentioning the salient feature for growth "No catalyst is required" as observed in many deposition methods". And what is the significance of Hitoshi's results and why it is a significant step for developing new nanodevices.

(III) Experimental details: Very clear and concise description of experimental set-up for growth process, structural characterizations, and wettability properties of GNSs.

(IV) Results and discussion: Clear explanation for the SEM images and TEM image (if possible) of GNSs fabricated by using CH<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> gases; we will help to produce the histograms for the morphology of GNSs (the number density, thickness, length, height, nearest distance between two GNSs), emphasising the factor of plasma species affecting the growth mechanism and consequently, tuning the wettability properties of as-deposited GNSs.

(V) Wettability properties:

- The comparison of wettability properties of GNSs produced by using the CH<sub>4</sub>+H-radical and C<sub>2</sub>F<sub>6</sub>+H-radical.
- The demonstration of ultimate control over the wettability properties of GNSs from hydrophobic to hydrophilic characteristic by Ar-plasma treatment. We could also demonstrate that this is a switch-over characteristic from CNTs where CNTs become more hydrophobic after Ar-plasma treatment in our experiments. We could help, contribute, and add some of our data in this section for the wettability properties of CNTs for explaining the switch-over properties.
- For illustrating more in-depth explanation, we could add some SEM images and few more histograms for the morphologies of GNSs before and after Ar-plasma treatments. If necessary, SEM images could be done here in Sydney.

(VI) Conclusions:

This opens up an exciting possibility to deterministically control the resulting morphology of 3-dimension CNWs patterns as well as their structural and electrical properties by a simpler adjustment of plasma process and excessively the control at the very early stage of nucleation.

(VII) Finally, we will help to prepare the best quality figures for the paper as follows:

**Figure 1:** Photo of experimental setup of our Plasma-CVD system and the schematic diagram of plasma-CVD, Ar-plasma treatment, and wettability experimental processes.

**Figure 2:** High-resolution SEM images of GNSs and correlated histograms for the thickness, length, height and nearest distance between two GNSs.

**Figure 3:** High-resolution TEM images for demonstration of highly active open graphitic edges of GNSs.

**Figure 4:** Micro-Raman spectra of GNSs (as-deposited by using precursor gases CH<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>).

**Figure 5:** The switch-over wettability properties of GNSs (as-deposited by using precursor gases CH<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>) as-treated with cold Ar-plasma treatment for 0 sec, 1 sec, 5 sec, 15 sec and 30 sec. – correlated with SEM micrographs of morphology and the associated histograms for the thickness, length, height and nearest distance between two GNSs for the samples treated with Ar.

# *What have I learned through ITP?*

## Knowledge

- How to write the paper
- How to present my study
- How to use the soft ware

## Experience

- For two months alone
- Different culture and customs
- Everyone who live in the world

For my PhD plan

## Not enough for me

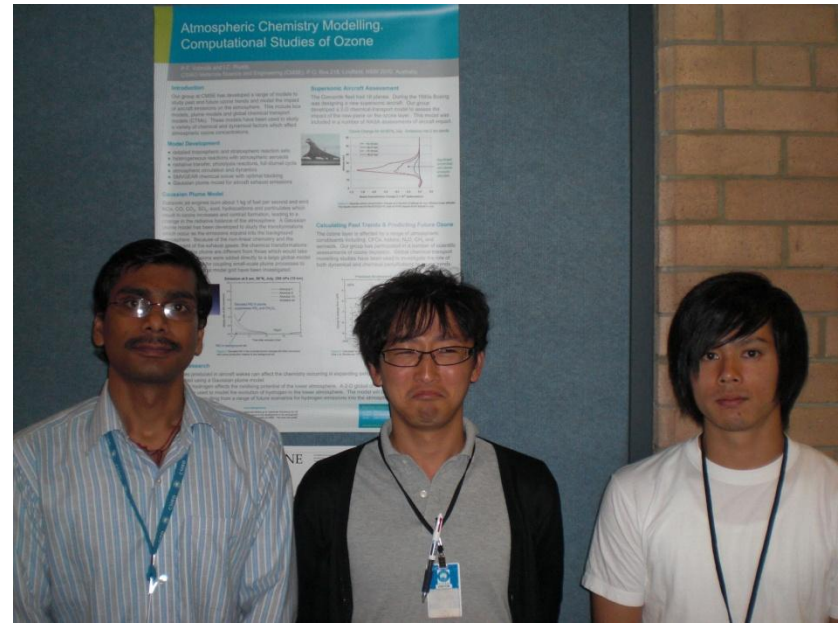
- Special knowledge
- Wide vision
- English skill (including ward and grammar)
- Positive attitude

## Language

- Ambition of English skill

*Thank you very much for your kind !!*

*I really appreciated Prof. Hori, Prof. Toyoda, Ms. Era and all stuff of CSIRO.*







# *ITP in this time*

Before we left Japan, I have gotten some mention they said.

- 1) they do some experiments in Japan and write a draft of a paper
- 2) they do all the safety etc. training as required
- 3) they observe the experiments without actually doing them on their own - but can engage later as contributors
- 4) they improve English and watch out culture and follow our approaches, work, safety, equipment design, etc.
- 5) they will have someone to supervise them but I will be able to talk to them maybe about once a week

We could not conduct the experiment in CSIRO. Because it will take half and a month to get a license in CSIRO to experiment.

- ✓ Discusses the result I brought from Japan.
- ✓ Making plan of PhD candidate.
- ✓ How to write the paper.