

出國報告（出國類別：國際會議）

參加第五屆國際表面科學與技術
會議心得報告

服務機關：國立雲林科技大學

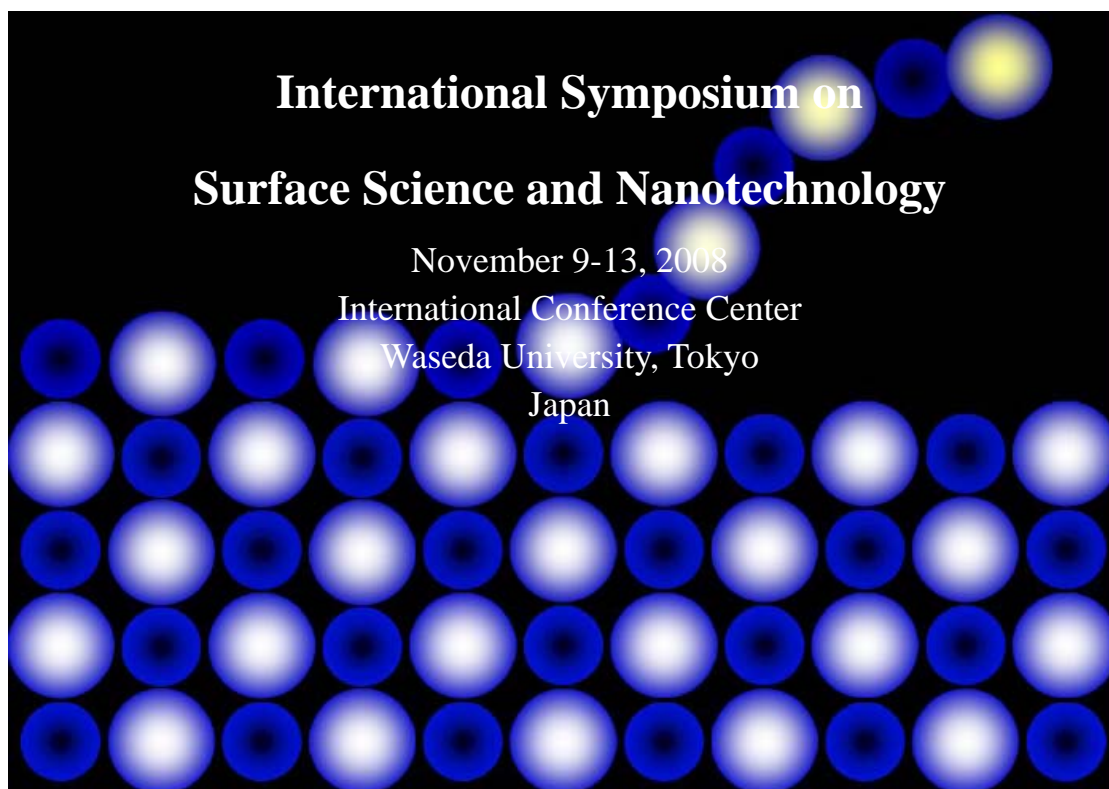
姓名職稱：林智汶 教授

派赴國家：日本

報告日期：97.11.25

出國時間：97.11.08 ~ 97.11.14

參加第五屆國際表面科學與技術會議心得報告



本屆大會 11/09~11/13 在日本東京早稻田大學 Waseda University 的 International Conference Center 舉行，大會主席由 Prof. I. Ohdomari 主持，Vice-Chair 分別為 K. Yoshihara (ULVAC PHI)，K. Takayanagi (Tokyo Inst. Technol.) 擔任。ISSS-5 係由日本表面科學會所主辦之第五屆國際會議，該會議每三年舉行一次。本會議主要在探討最新的奈米科技相關的表面科技。主要的主题包括：Theory and dynamics, fabrication and application of nano-structures and nano-materials, novel characterization methods, and chemical and biological applications. 並且鼓勵針對未來發展發向進行研習與討論。其中

Theory and dynamics 部份包括：

- Theoretical approaches to surface/interface and nano-structures and properties
- Surface structures: atomic and electronic structures, and surface vibrations
- Surface dynamics: adsorption, desorption, reaction and diffusion

Fabrication and physical properties 部份包括：

- Atomic-scale controlled surface/interfaces and self-organized nanostructures

- Nano-materials: nanotubes, nanowires, nanoparticles and nanodots
- Fabrication processes: epitaxy, deposition, etching, cleaning and thin-film growth
- Device applications of metal, ceramics, organic and hybrid films

Characterization methods 部份包括：

- Characterization of surfaces, interfaces and nanostructures
- Tools and standards for micro/nano-analysis
- Scanning probe microscopy

Surface chemistry 部份包括：

- Colloid chemistry and soft materials: supramolecules, macromolecules and liquid crystal
- Electrochemistry, photochemistry and catalysis
- Self-assembly and self-organization for nanostructure formation and characterization

Biological applications of surface science and nanotechnology 部份包括：

- Nanobio-processes, biosurfaces and biointerfaces
- Bio-diagnostics, bioassays and biosensors

會議的議程如下：

November, 2008

9 (Sun) 3:00pm-6:00pm.....	Registration and Get-Together
10 (Mon) 9:00am-8:00pm.....	Scientific Sessions
11 (Tue) 9:00am-5:45pm.....	Scientific Sessions
6:00pm-8:30pm.....	Banquet (RIHGA ROYAL HOTEL)
12 (Wed) 9:00am-8:00pm.....	Scientific Sessions
13 (Thu) 9:00am- 6 :30pm.....	Scientific Sessions

議程密集又冗長是本會議的特色，每天都開到晚上，不過像11月11日大會特地安排在 RIHGA ROYAL HOTEL 進行大會晚宴，讓大夥在辛苦開會學習與討論之餘，也能進行國際交流，相互輕鬆交談。

大會安排的 Plenary 演講包括：

- **Patrick Soukiassian** (Univ. de Paris-Sud/Orsay)
Engineering and Understanding Surface, Interfaces and Nanostructures Properties at the Atomic Scale
- **Yasuhiro Iwasawa** (Univ. of Tokyo)
In-situ Surface Science of Dynamic Catalysis: Active Organized Structure and Reaction Genesis at Surfaces
- **Wolfgang Knoll** (Max-Planck-Institute for Polymer Research)
Interfacial Architectures for Bio-Sensing

大會邀請的演講包括：

Theory, structure and dynamics

- (A) Theoretical approaches to surface/interface- and nano-structures and properties

- Mads Brandbyge (Tech. Univ. of Denmark)
Theoretical studies of electron transport in nano-scale systems
- Alessandro De Vita (King's College London)
Modelling the self-assembly of supported supramolecular nanostructures
- Mineo Saito (Kanazawa Univ.)
Half-metallicity of Carrier-doped Armchair Graphene Nanoribbon

- (B) Surface structures: atomic and electronic structures, and surface vibrations

- Ulrich Heiz (Tech. Univ. of Munich)
Size-dependent chemistry of supported clusters
- Natarajan Chandrasekhar (Nat'l Univ. of Singapore)
BEEP - probing technologically important interfaces with nanometer spatial resolution
- Kota Tomatsu (Univ. of Tokyo)
Scattering potentials of Si and Sn atoms embedded into Ge (001) studied by STM and ab-initio calculations

- (C) Surface Dynamics: adsorption, desorption, reaction, and diffusion

- Andrew Hodgson (Liverpool Univ.)
The Structure and Reactions of Water and OH at Metal Surfaces
- Hiroshi Morikawa (Kyoto Univ.)
Tunneling dynamics of single-molecule tautomerization

Fabrication and physical properties

- (D) Atomic-scale controlled surfaces/interfaces, and self-organized nanostructures

- Sebastian Loth (Andreas Heinrich) (IBM)
Quantum magnetism and spin coupling at the atomic scale
- Richard Berndt (Univ. of Kiel)
Conductance of controlled single atom and single molecule contacts

- (E) Nano-materials: nanotubes, nanowires, nanoparticles, and nanodots

- Chuan Liang Feng (Max Plank Inst.)
Quantum-Dot/Dendrimer Based Functional Nanotubes for Sensitive Detection of DNA Hybridization
- Kenji Hata (AIST, Japan)
Super-Growth CVD for Mass production of Carbon nanotubes and its applications
- Nan Wang (Univ. of Cambridge)
*Direct measurement of charge transport through single conducting polymer molecule
wired into gaps in single walled carbon nanotubes*
- Takami Muto (Tohoku Univ.)
*The Formation Mechanism of Aluminum Nanodots by Inhomogeneous Anodization
as a Self-Alignment Technique for a Room-Temperature Operating Single-Electron Transistor*

- (F) Fabrication processes: epitaxy, deposition, etching, cleaning, thin-film growth

- Masaharu Oshima (Univ. of Tokyo)
In-situ photoelectron spectroscopy and photoemission electron microscopy for local electronic and magnetic structures of transition metal oxide thin films
- Kenji Shiraishi (Univ. of Tsukuba)
What happens at nano-scale interfaces?
- Wei-Chuan Fang (Industrial Tech. Research Inst., Taiwan)
Low-Temperature Synthesis and Characterization of ITO Thin Films

- (G) Device application of metal, ceramics, organic, and hybrid films

- Masakazu Nakamura (Chiba Univ.)
Limiting Factors of Carrier Transport in Organic TFTs with Polycrystalline Active Layer

Characterization methods

- (H) Characterization of novel surfaces, interfaces and nanostructures

- Michel A. Van Hove (City Univ. of Hong Kong)
Nanostructure from Scanning Tunneling Microscopy and Low-Energy Electron Diffraction
- Shirley Chiang (Univ. of California-Davis)
High Resolution Surface Microscopy of Nucleation, Growth, and Phase Transitions
- Taku Suzuki (NIMS, Japan)
Element selective spin state analysis at surfaces and interfaces by spin-polarized ion scattering

- (I) Tools and standards for micro/nano-analysis

- Thomas Schmidt (Fritz-Haber-Institute in Berlin)
SMART: using an aberration corrected photoemission electron microscope as a nano-analytic tool
- Hiroshi Daimon (NAIST, Japan)
Two-dimensional photoelectron spectroscopy by a conventional and newly-developed display analyzer

- (J) Scanning probe microscopy

- Hirofumi Yamada (Kyoto Univ.)
Subnanometer-resolution Imaging of Biomolecules and Hydration Force Measurements by Frequency Modulation Atomic Force Microscopy
- Holger Schönherr (Univ. of Twente)
Chemical and Optical Probing of Nanoscale Soft Materials by AFM Approaches: Challenges, Hopes and Opportunities

Surface chemistry

- (K) Colloid chemistry and soft materials: supramolecules, macromolecules, and liquid crystal

- Satomi Onishi (Univ. of South Australia)
Friction and capillary forces at the nanometer scale
- Masatsugu Shimomura (Tohoku Univ.)
A Novel Nano Bio-interface Prepared by Self-organization

- (L) Electrochemistry, photochemistry and catalysis

- Charles T. Campbell (Univ. of Washington)
Thermodynamics and Kinetics of Elementary Steps in Catalysis

- (M) Self-assembly and self-organization for nanostructure formation, and characterization

- Atsushi Takahara (Kyushu Univ.)
Molecular Design and Characterization of Soft Interfaces
- Li-Jun Wan (Chinese Academy of Sciences)
Surface Molecular Engineering: From Single Molecule to Self-assembly

Biological applications of surface science and nanotechnology

- (N) Nanobio-process, biosurfaces and biointerfaces

- Robert Hamers (Univ. of Wisconsin-Madison)
Ultra-stable Molecular and Biomolecular Interfaces via Covalent Grafting

- (O) Bio-diagnostics, bioassays and biosensors

- Andreas Offenhäuser (Research Center Jülich)
Connecting DNA, Protein and Neurons with Electronics
- Hiroshi Kawarada (Waseda Univ.)
Mechanism of DNA and RNA sensing by diamond surface channel devices

本職此次參予口頭報告，被安排在 1 1 月 1 0 日星期一的下午 5 : 4 5 ~ 6 : 0 0 ，

1400	Y. Amano <i>Surface</i>	Introductory	T. Schmidt	SMART: using an aberration corrected photoemission electron microscope as a nano-analytic tool (invited)	L.-J. Wan <i>SelfAssem</i>	Surface Molecular Engineering: From Single Molecule to Self-assembly (invited)	H. Schöberl <i>SPM</i>	Chemical and Optical Probing of Nanoscale Soft Materials by AFM approaches: Challenges, Hopes and Opportunities (invited)
	K. Nozoyori <i>Graphene 982</i>	Physics and Applications of Graphene (invited)	Tools					
1500	M. Kusunoki <i>Graphene</i>	Formation of uniform carbon nanotube films and graphene on SiC (invited)	T. Sasaki <i>Tools 998</i>	Transmission electron diffraction by low energy electron beam emitted from a single-electron electron source	K. Kawaga <i>SelfAssem 977</i>	Allyl Monolayers on Si(111) Observed by High-resolution Surface-Resolved Raman Scattering Spectroscopy	Y. J. Li <i>SPM 1009</i>	Development of Multi-Functional High-speed Phase Modulation AFM in Liquids
	M. Nihei <i>Graphene</i>	Multilayer Graphene for Interconnect applications (invited)	J. Otsuki <i>Tools 999</i>	Characterization of field-emitter W tip fabricated by field-assisted etching	Mid. Z. Hossain <i>SelfAssem 981</i>	Acetophenone, a unique example of organic molecules in growing 1-D molecular assemblies on the Si(100)-(2x1)-1x1 surface	Y. Sugawara <i>SPM 1004</i>	Atom Manipulation on Cu(110)-O Surface with Low Temperature Noncontact AFM
1600	M. Nihei <i>Graphene</i>	Multilayer Graphene for Interconnect applications (invited)	Y. Morita <i>Tools 1200</i>	AFM measurement of etched Si surface etching by oxygen molecule	C. Rabot <i>SelfAssem 973</i>	Self-assembly of meta-aminobenzoate on Cu(110) investigated with scanning tunneling microscopy and X-ray absorption spectroscopy	M. Hamada <i>SPM 1103</i>	Nano-scale lithography with frequency-modulation atomic force microscopy
	M. Nihei <i>Graphene</i>	Multilayer Graphene for Interconnect applications (invited)	H. Daitom	New photoelectron spectrometer to measure two-dimensional angular distribution and mapped sample images (invited)	A. M. Caro <i>SelfAssem 986</i>	Engineering self-assembled monolayer as copper diffusion barrier Cu/NiO-Si/SiO ₂ interface	P. Yamada <i>SPM 775</i>	Electric Dipoles of Surface Nano-Structures on Insulating Substrates
Break								
1615	C. Ohshima <i>Graphene</i>	To be announced (invited)	T. Suzuki <i>Character 1009</i>	Element selective spin state analysis at surfaces and interfaces by spin-polarized ion scattering (invited)	A. Takahara <i>SelfAssem</i>	Molecular Design and Characterization of Soft Interfaces (invited)	H. Yamada <i>SPM</i>	Subnanometer-resolution Imaging of Biomolecules and Hydrogen Force Measurements by Frequency Modulated Atomic Force Microscopy (invited)
	H. Hibino <i>Graphene 1122</i>	Local work function measurements of epitaxial few-layer graphene (invited)	K. Ueda <i>Character 1009</i>	Image contrast of ESD ions from p-n Junction of As-implanted Silicon Surface Studied by Hydrogen	K. Murakoshi <i>SelfAssem 110</i>	Novel Molecular Filter using Metallic Nano-gate	T. Matsumoto <i>SPM 1105</i>	Three-resolved electrostatic force detection by frequency shift mode
1715	T. Ando <i>Graphene</i>	Basic electronic and transport properties of graphene and nanotube (invited)	S. Kitayama <i>Character 1010</i>	Radiation-induced Luminescence from Au, Pt/CdZ by 10 keV He and He ⁺ Ion Irradiation	K. IKEDA <i>SelfAssem 981</i>	Cap-nuclei enhanced Raman spectroscopy for self-assembled monolayers on single crystalline metal surfaces	M. Coenen <i>SPM 709</i>	Molecular catalysis studied by (EC)-STM
	H. Kagetsuna <i>Graphene 998</i>	First principles study on Epitaxial Graphene Formation on SiC (0001) Surfaces (invited)	J.D. Hwang <i>Character 1011</i>	Highly coherent electron sources: noble-metal covered Pt(111) single atom type	T. Miyasaka <i>SelfAssem 977</i>	Two-color nan-frequency generation study of single-walled carbon nanotubes on silver	T. Nishio <i>SPM 1209</i>	Vortex states in nano-size Pb island structures studied by LT-STM/STIS
1815			A. Otsuki <i>Character 1011</i>	Calculation of forces acting on an electrode during particle size measurement by interactive force apparatus under the electric field	Y. HORIUCHI <i>SelfAssem 977</i>	Preparation of Transition Metal Oxide-containing Mesoporous Silica Thin Films Using Various Structure Directing Agents and Their Unique Surface Properties	K. Honma <i>SPM 1000</i>	Atomic Configuration, Conductance and Strength of Atomic-Sized Hydrogen Molecules
			C.-W. Lin <i>Character 1011</i>	Surface Thermodynamics of the Chemically synthesized polypyrrole and polyaniline nanofibers and their gas-sensing responses to STEC compounds	Y. BABA <i>SelfAssem 110</i>	Microscopic observations of electronic structure and molecular orientation for phthalocyanine thin films by X-ray-extended PEEM	K. Kikuchi <i>SPM 891</i>	A Scanning Tunneling Microscopy Observation of rectifying (rect) / Reconstructed (rect/rect) Surface
			S. BOYABOUBA <i>Character 1011</i>	Characterization of Residue Sputtered Molybdenum Oxide Thin Films for Gas Sensors	A. Tomoka <i>SelfAssem 977</i>	Selective Formation of Dispersed Quasi-Stable Aggregates of Rhodamine: Comparison with J- and H-Aggregates	K. Goto <i>SPM 891</i>	Detecting vibrational excitation probabilities with sub-Angstrom resolution

報告的題目是：Surface thermodynamics of the chemically synthesized polypyrrole and polyaniline nanofibers and their gassensing responses to BTEX compounds

內容如下：

Surface thermodynamics of the chemically synthesized polypyrrole films and their gas-sensing responses to BTEX compounds

Y. L. Liu, C. W. Lin*
Department of Chemical and Materials Engineering
National Yunlin University of Science and Technology, Yunlin, Taiwan
E-mail: lnow@yuntech.edu.tw

Background

- Considerable quantities of volatile organic compounds (VOCs) are produced from industrial sources such as printing and coating facilities, foundries, electronics and paint manufacturing units.
- A group of VOCs, including aromatic hydrocarbons such as benzene, ethylbenzene, toluene, and xylene (commonly referred to BTEX), are widely used in industry and poses serious adverse effects on the quality of air.
- The utilization of conducting polymers as gas sensors for detecting these highly health-threatening VOCs may be a promising approach.

Microscopic Gas-Sensing Model based on Langmuir isotherm

The overall resistance of the sensing film can be regarded as the paralleling of several pseudo-monolayers and each layer is composed of several resistors in series.

$$\frac{1}{\Delta R_t} = \frac{n}{m(r_1 - r_0)} + \frac{n}{m(r_1 - r_0)K_m} \frac{1}{C_{ad}}$$

m: number of active site per monolayer
n: thickness of the thin film
 ΔR_t : resistance change before and after gas sorption
 K_m : Adsorption Equilibrium Constant
 C_{ad} : Concentration of the detected gas
 r_1, r_0 : site resistance as the site is occupied and vacant

To plot (1/ ΔR_t) vs. (1/ C_{ad})

> The value of $[m(r_1 - r_0)]/n$ (regarded as secondary doping efficiency) can be determined from the reciprocal of the intercept and K_m can be obtained by dividing the intercept by the slope.

Chemically-polymerized PPyCl sensors exposed to BTEX compounds

- The effect of adsorption affinity (K_m) and the doping efficiency ($[m(r_1 - r_0)]/n$) could be distinguished and calculated in terms of adsorption equilibrium constant.

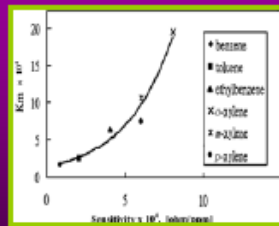
The values of sensitivity, K_m , and $m(r_1 - r_0)/n$ for BTEX vapors detected by PPyCl sensor

Vapors	Sensitivity (Ω/ppm)	K_m	$m(r_1 - r_0)/n$ (Ω)
Benzene	8×10^{-5}	1.72×10^{-4}	-0.44
Toluene	2×10^{-4}	2.50×10^{-4}	-0.91
Ethylbenzene	4×10^{-4}	6.50×10^{-4}	-0.70
o-Xylene	8×10^{-4}	1.97×10^{-3}	-0.44
m-Xylene	6×10^{-4}	1.07×10^{-3}	-0.54
p-Xylene	6×10^{-4}	7.45×10^{-4}	-0.71

> K_m :
o-xylene > *m-xylene* > *p-xylene* > *ethylbenzene* > *toluene* > *benzene*

> Sensitivity:
o-xylene > *m-xylene* > *p-xylene* > *ethylbenzene* > *toluene* > *benzene*

K_m vs. sensitivity for BTEX vapors to PPyCl sensors



> The sensing ability of PPyCl polymer film is dominated by the affinity of the compound to the sensing material rather than the secondary doping level by the detected compound.

- Is it possible to have a directly experimental proof to the remark obtained from the resistance measurements that the affinity of the detected vapor to the sensing material dominates the sensitivity of the gas sensor?

Surface Properties of Conducting Polymers

- Inverse Gas Chromatography (IGC) have been used to investigate surfaces of conducting materials. It appears to be particularly useful for determining the sorption properties of molecules on surface.
- We are intending to present some preliminary results obtained by using IGC technique subjected to the relationship of the surface interaction force and the sensing response.

Measurements of IGC data

- > In IGC, measurements were carried out at infinite probe dilution, i.e. approximately zero sorbent surface coverage, ensure that the results obtained from the experiments apply exclusively to adsorbate-adsorbent interactions.
- > The retention time of the probe, t_r , the time it takes the probe to travel through the column, can be converted to the net retention volume V_N by

$$V_N = JF(t_r - t_0) = JFt_R$$

where F is the carrier gas flow rate and t_0 is the net retention time. J is the correction factor of pressure gradient for mobile phase

Relation of ΔG_a and V_N

- The net retention volume, V_N is related to the free energy of adsorption, ΔG_a ($J \text{ mol}^{-1}$) by :

$$\Delta G_a = -RT \ln(V_N) + C$$

where R is the gas constant, T is the column temperature, and C is a constant which takes into account the weight and specific surface area of the packing material and the standard states of the probes in the mobile and the adsorbed states.

- Manipulation of ΔG_a (or $RT \ln V_N$) data for the various probes leads to the evaluation of γ_s^d , the dispersive contribution to the surface energy of the materials.
- A standard method to evaluate the dispersive component of the surface energy relies on the retention data of the n-alkane series.

Dispersion component of surface energy for PPy determined at three temperatures

	Temperature (K)		
	443	433	423
γ_s^d (mJ/m^2)	69.96	72.10	74.73

- > Increase in the kinetic energy of the adsorbed molecules on the surface would cause decrease in the surface energy
- > PPyCl is a high surface-energy material compared to conventional polymers, advantageously to be used to fabricate sensors with better sensitivity

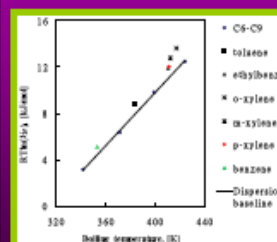
Specific Interactions

- If both dispersive and specific interactions are operative at the gas/solid interface, it is assumed that they contribute to the total ΔG_a in an additive manner:

$$\Delta G_a = \Delta G_a^d + \Delta G_a^s$$

where d and s are referred to dispersive and specific interactions, respectively. Several approaches were proposed to distinguish between ΔG_a^d and ΔG_a^s

Plot of $RT \ln(V_N)$ vs. boiling point for alkanes and BTEX probes adsorbed onto PPyCl

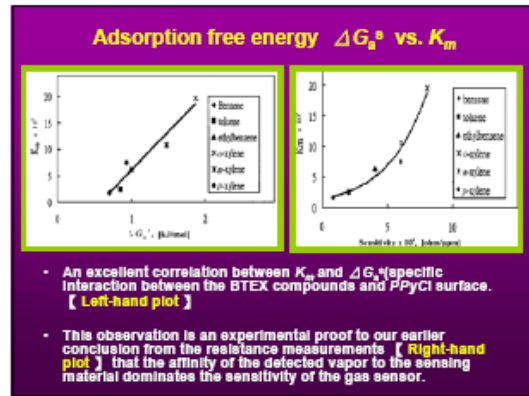


- We use the traditional approach: ΔG_a values are related to the boiling point of the injected probes.
- The n-alkanes series lead to a linear plot which constitutes a reference for London dispersive interactions
- The marker corresponding to the BTEX compounds are located off the baseline, from which the specific interaction ΔG_a^s can be determined.

Values of ΔG_a , ΔG_a^* , and ΔG_a^{\ddagger} for BTEX adsorbed on to PPyCl

ΔG [kJ/mol]	Benzene	Toluene	Ethylbenzene	o-Xylene	m-Xylene	p-Xylene
ΔG_a	5.12	8.79	11.93	13.61	12.68	12.02
ΔG_a^*	4.42	7.94	10.94	11.75	11.21	11.06
ΔG_a^{\ddagger}	0.70	0.85	0.99	1.86	1.47	0.94

• Surface free energy ΔG_a^* shows an order of o-xylene > m-xylene > p-xylene \approx ethylbenzene > toluene > benzene

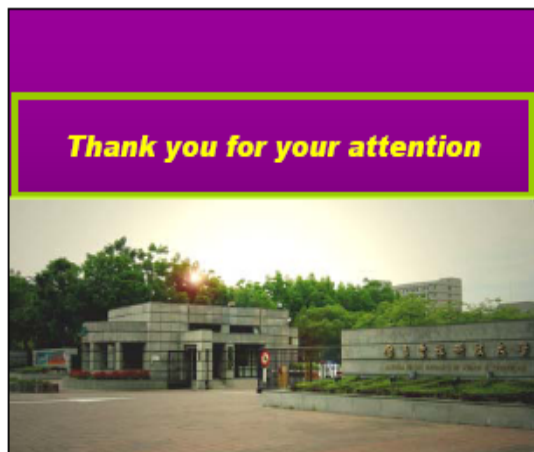


Conclusions(I)

- The sensing responses of the Cl-doped PPy sensors towards BTEX compounds were investigated by measuring the resistance change of the film.
- The adsorption equilibrium constant, K_m , according to the adsorption theory were in a magnitude order of o-xylene > m-xylene > p-xylene > ethylbenzene > toluene > benzene. A good correlation between the sensitivity and K_m values was obtained.

Conclusions(II)

- A good correlation between the adsorption equilibrium constants, K_m , and specific component of adsorption free energy, ΔG_a^* , substantiate the fact that the affinity (i.e. the coverage) of the detected BTEX vapor to the sensing material dominated the sensitivity of the gas sensor in the present work.



報告完畢後，得到很好的迴響，主持人評為相當出色的報告（Excellent presentation），個人也認為報告得相當成功，也在一次為我國學術界爭取高度曝光的機會。



日本東京早稻田大學 International Conference Center

總結本次參加在日本東京稻田大學舉辦之 ISSS-5 國際會議，對於日本人組織的能力相當讚賞，就如日本人發明的產品一般，小巧精緻非凡，雖然不若歐美國家動輒十幾個演講廳同時舉行的規模，非但沒有炫麗的大會佈置 而且還樸實的令人驚訝，如下圖的海報夠樸實了吧！



但大會將心思花在研討內容的品質提昇，反而更能凸顯焦點及引發參與者的興趣，發現絕大多數台灣來的與會者都全神貫注地參加，相信大家再短短五天的會議都有不錯的收穫，也做了互動良好的學術交流。