

國家同步輻射研究中心
出國報告書

出國人姓名：王嘉興、楊耀文

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目的地 (國家、城市)：德國、柏林

參加會議名稱或考察、研究訓練地點：

5th Annual Ambient Pressure X-ray Photoelectron
Spectroscopy (APXPS) Workshop (APXPS- 2018)

(請自下一頁開始撰寫)

一、目的

參與 5th Annual Ambient Pressure X-ray Photoelectron Spectroscopy Workshop 會議，發表近期於近室壓 X 光光電子能譜實驗站的研究成果，另外也與各國研究 APXPS 的專家學者交流分享最新的發展趨勢。

二、行程

12/09-12/10 從新竹到德國柏林

12/11- 12/14 在柏林 Harnack-Haus 參加會議議程

12/14- 12/15 從德國柏林回到新竹

三、內容摘要：

本次 5th Annual APXPS workshop 會議在德國柏林的 Harnack-Haus 舉行，Harnack-Haus 是為 Max Planck Society 固定舉辦會議的地點，有許多的偉大科學家都曾經到此地參加會議，並被標註於會議大廳的牆面上，因此能夠在這個地方參加會議令我感到非常高興。此次會議依上次會議的決定，於 12/12 正式會議前一天下午先行註冊然後隨即舉辦技術分享討論會，技術分享會包含了六大主題 1.利用 Tender X-ray 當作激發光源探討固液介面的反應、2.探討具有 Spatially resolved APXPS 技術、3. SPECS 廠商報告、4.討論 Charge compensation 的問題、5. 一大氣壓下的 APXPS 技術、6. Cross contamination 問題。接著連續三天的會議議程，皆從早上九點開始下午五點結束，其內容包含了理論計算、電化學反應、催化反應與不同材料界面反應研究等，而最後一天下

午則是參觀德國同步輻射研究中心(BESSY)。本次會議來自台灣的人員，除了本中心兩位代表參加之外，APXPS 實驗站用戶淡江大學莊程豪教授也一起前往此次會議。

四、心得概述與建議

今年為第五屆的近室壓 X 光光電子能譜國際會議，此會議讓使用此技術或發展此項技術的專家學者能夠聚在一起討論並分享目前最新技術發展與研究的狀況，使我們正在發展此項技術的國家有學習的機會是相當難能可貴的。此次會議有別前面幾次會議多加了技術發展分享的會前會，其中討論到 charge compensation 議題與 cross contamination 問題都與我們目前研究及實驗站常碰到的問題息息相關，透過參加此次會議直接了解目前各國如何處理樣品 charging 的方式，提供了我在於發展 charge compensation 的方法做為參考。在 cross contamination 問題，與會專家也分享了幾個改善方式，讓我了解到不同汙染源的來源，並知道如何避免，這些實驗上小細節是無法從文獻上讀取到的，唯有透過面對面溝通及此技術分享才能獲得，讓我學到不少東西。

Organizers of this year's workshop put forward a program of rather different format due to the requests for having a dedicated technical session before the start of science sessions. Beginning on the first day of the workshop (12/11), Ethan Crumlin of ALS started with a talk on the issues related to the use of tender X-ray for APXPS. He laid out several topics for the audience to discuss on: 1) where are tender APXPS systems being developed? 2) what type of science are being pursued? 3) windows or no windows? 4) what are good techniques to combine with tender APXPS, and 5) what are capabilities scientists would be interested in? So far, there are only a handful of facilities providing synchrotron-based tender X-ray (4 to 6 keV) for APXPS experiments and they include BESSY II, ALS, and SSRL. One big

advantage of having 4 keV X-ray is to have a large penetration depth for the water film that is composed of light elements of H and O, resulting in a large inelastic mean free path up to 3 nm for 4 keV X-ray, and rendering the electrochemical interface experimentally observable. If synchrotron tender X-ray unavailable, a combination of synchrotron soft X-ray and fixed energy, X-ray tube sources like Cr K α line with energy of 5.4 keV or Ag L α line of 3 keV is also highly desirable, an approach taken by Pohang light source and others. We worked on a possible addition of Ag L α source to augment our machine capability in the beginning of the year but eventually abandoned this approach due to the weaker flux of Ag source and a lack of suitable ports in our machine. As the employment of tender X-ray APXPS is in the nascent stage, we expect to see more broadened applications in the years to come, as happened in HAXPES technique. Meanwhile, we envisage that an employment of tender X-ray offers a more robust window solution for vacuum isolation since tender X-ray can penetrate through Be or thicker/ durable Si₃N₄ window. If a continuous energy scanning in tender X-ray is made available, then it will be possible to perform interesting XAS experiments covering the useful biochemically important elements of S and Cl. Regarding our existing APXPS endstation, its relocation to TPS has been included in the third-phase TPS beamline construction plan. The construction project of new beamline and endstation needs to be blueprinted in 2019. Whether we need tender X-ray for APXPS will be an issue of interest to electrochemical research community. We need to take on the work and keep abreast with the newest development in tender X-ray APXPS.

Another issue that has been receiving the attention of APXPS community is whether it is a viable option to perform spatially resolved APXPS imaging. Workshop organizers recognized this issue by asking Zeller to moderate a discussion session. XPS imaging in UHV by means of selective area mapping via the electron optics of the energy analyzer has been a mature technique with a “best spatial resolution” of a few microns. Therefore, it should not be too much a problem to extend this technique to ambient pressure range. However, it will be of even greater impact if the existing spatially resolved imaging XPS methods like SPEM can be adapted into high working pressure environment because their proven spatial resolution is superior to that based on electron optics. In this regard, it is worth noting that Electra synchrotron has implemented several schemes to work on samples under different environments.

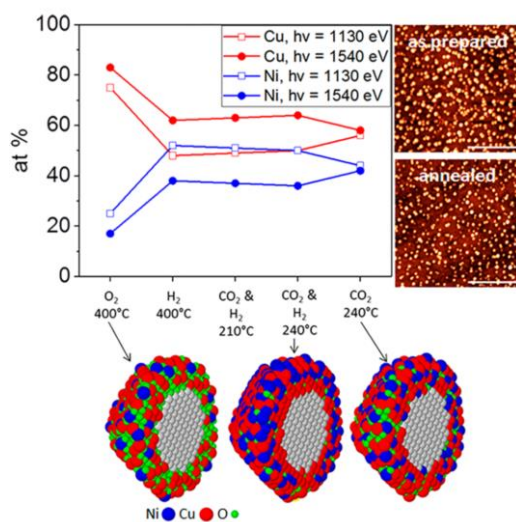
Karslioglu led the discussion on charge compensation, an increasingly important area coupled to the promulgation of APXPS. It is now well established that the presence of gaseous molecules in ambient pressure can alleviate the charging problem intrinsic to the XPS measurements of non-conducting samples because the electrons and ions produced by the photoionization of ambient gases can charge-neutralize the trapped photo-holes in the samples. It is noted that in ambient pressure environment of APXPS, the conventional charge compensation by flood guns cannot be applied due to an immediate filament burnout problem. One remedy is to use a differential pumping floor gun, a project being actively pursued. A successful application of this charge-neutralization by ambient gases sees the recent

emergence of XPS spectra taken from exotic samples like leaves, bacteria, etc., which really extends XPS technique to heretofore unthinkable areas of applications. However, it needs to be cautioned that the charger neutralization by photoionized gas molecules works in principle, but in practice it is very tricky to apply, an opinion echoed by the audiences as well. We found that the amount of charge compensation by gases is either under or over or zero at all. We also realized that we needed to pay attention to the instrument layout around the sample as well in order to have a satisfactory charge compensation. A few months back, we started to play around the technique by using different gases of different pressure as well as applying biasing voltage to the different points around samples, and concluded that the charge compensation scheme by gases worked to some degree but not perfectly. We now plan to bring the X-ray entrance tube terminated with a Si_3N_4 membrane even closer to the sample, from 7 cm down to 3 cm so that many more charge species can be made available to neutralize the trapped photo-holes.

Juan Velasco-Velez presented an APXPS measurement with the sample kept at one bar pressure and the pressure isolation between the sample and the APXPS analyzer is achieved with single-layer graphene supported mechanically by holy Si_3N_4 membrane. The graphene layer stops the gas transmission but allows the passage of photoelectrons. Fully developed and reliable SL graphene devices will open up many applications in areas such as liquid cells, ambient pressure gas cells for SPEM, PEEM, TEM usage. We had some limited, unsuccessful experiences in fabricating SL graphene cells and we might revisit the fabrication

of the graphene cells in the future.

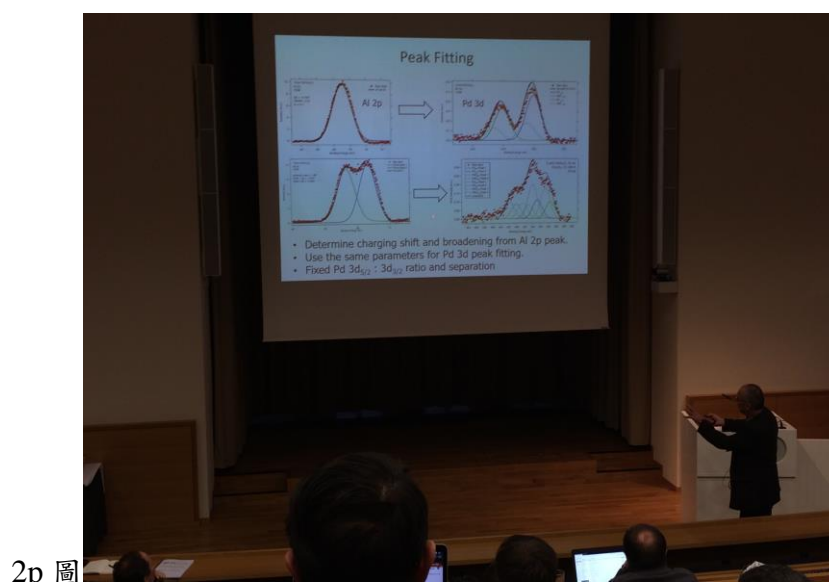
以下是參與此次會議聆聽 keynote talks、invited talks、與 oral contributions 的部分心得。首先是來自 Department of Interface Science, Fritz-Haber Institute of the Max Planck Society 的 Beatriz Roldan Cuenya 教授主講環境影響奈米催化顆粒的結構組成成分的變化，她講述不同的奈米雙合金顆粒如 CuZn、CuNi、NiGa 等不同材料在不同氣氛與溫度下其材料結構成分的變化，以 CuNi 奈米顆粒為例(如圖一)，她利用不同的同步輻射光能量，以及在不同溫度與環境氣氛下，可以觀測到雙金屬元素會有不同的分離行為，尤其是在做二氧化碳氫化反應的條件下($\text{CO}_2 + \text{H}_2$, Temp=210- 240 度)，可以看到 Ni 金屬會擴散到雙金屬顆粒的表面，驗證了可以提高 methanol 生成反應的因素。此研究與個人所從事的奈米雙金屬顆粒催化研究極為相關，對於我的未來研究方向有很大的幫助。



圖一: Beatriz Roladan Cuenya 教授所講的 CuNi 奈米顆粒於不同溫度環境氣氛下的結構成分變化。(J. Phys. Chem. B 2018, 122, 919–926)

來自 Diamond Light Source 的 Georg Held 教授講述了利用 APXPS 技術臨場探討成長在 Al_2O_3 support 的 Pd 奈米顆粒在催化 methane 氧化成一氧化碳或二氧化碳的過程。

我們都知道氧化鋁的 bandgap 大約為 7 eV，相當的不導電，因此收取光電子能譜一定會碰到 charging 的現象，使能譜往高束縛能位移，一般 in-house X-ray 光源則會透過 flood gun 去中和表面的正電荷並且以碳譜的位置作為能量校正的方式。然而目前的 APXPS 系統並無配備 flood gun，且如果是利用同步輻射光當光源，其光源強度可以因光束線的參數設定而改變，並無法有效的消除 charging 的現象。然而進行 APXPS 實驗時，分析腔體會引入大量氣體，激發光源也可以激發腔體中的氣體產生電子與離子，此時電子有機會去補償樣品表面 charging 的地方，減少 charging 的程度。然而 Georg Held 他們的實驗在低溫下其圖譜依舊有 charging 的現象，因此他們利用擬合有 charging 現象的 Al



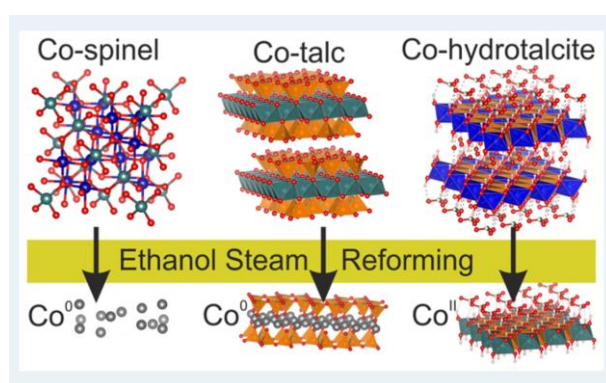
2p 圖

圖二. Georg Held 教授講述利用擬合有 charging 現象的 Al 2p 圖參數來 fitting Pd 3d 能譜的投影片。

譜，然後再將擬合的參數將套入 Pd 3d 的圖譜中，如圖二。解決了他們一開始在低溫下能譜會 charging 的分析問題，而其在高溫下能譜則不會 charging 的情形產生，他提出 ion hopping 的機制，雖然現場還是有人提出質疑，但目前大家也沒有很好的解釋，是還有可以討論的空間。解決 charging 能譜的解釋方式，他們的實驗可以很看到 Pd 奈米顆粒在一開始溫度在 550- 650 K 時會先被氧化形成 PdO，然後在高溫時(700 K)又會被還原

回來形成 Pd 金屬態，透過一系列的研究他們確定 5- 10 nm 的奈米顆粒可以在較低的溫度進行部分甲烷氧化反應並發表結果於國際期刊上。其觀測的 charging 現象與我我在進行一些較不導電的樣品實驗時也有看到相同現象，目前也是無法提出很好的解釋，相信未來經過大家的不斷努力討論會有一致的解釋產生。

而來自 ALBA Synchrotron Light Source 的 Carlos Escudero 教授講述了 Co-based 催化劑在於 ethanol steam reforming 的臨場 APXPS 與 XANES 的研究。他講述了利用 Co-based 催化劑可以降低 ethanol steam reforming 的反應溫度，然而大部分的 Co-based 催化劑都會在催化反應後失去活化，主要原因是因為反應過程大多數的 Co-based 催化劑會產生鈷金屬，使得碳沉積於催化劑表面，使其失去活性。作者透過與 University Politecnica de Catalunya 的 Jordi Llorca 教授合作，取得三種不同的 Co based 催化劑，分別為 Co_3O_4 (Co-spinel)、 $\text{Co}[\text{Si}_2\text{O}_5](\text{OH})_2$ (Co-talc)、 $[\text{Co}_2\text{Mg}_4\text{Al}_2(\text{OH})_{16}]\text{CO}_3 \cdot 4\text{H}_2\text{O}$ (Co-HT) 如下圖三，他們在乙醇與水(1:6)的氣氛下於不同的反應溫度下進行能譜收集，發現 Co_3O_4 在反應溫度為 500 度以上則會完成轉變成 Co 金屬，然而 Co-talc 樣品則會部分析出形成 Co 金屬，而 Co-HT 此樣品則可以耐熱到 580 度都不會有 Co 金屬的產生，將有助於 ethanol steam reforming 的進行。

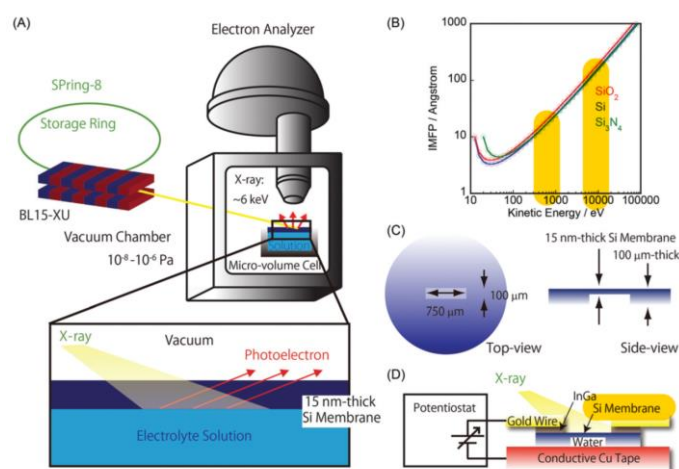


圖三: Carlos Escudero 教授所使用的不同三種 Co based 催化劑。

(ACS Catal. 2018, 8, 9625–9636)

來自 Hokkaido University, Japan 的 Takuya Masuda 教授講述他們自行發展的電化學

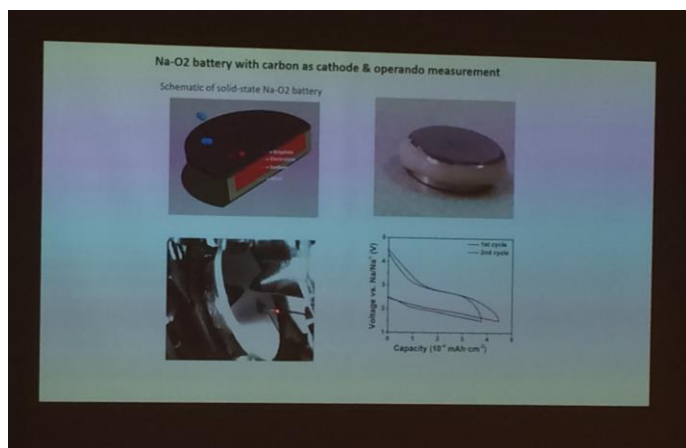
cell(如圖四)用於光電子能譜的研究，首先他們於 2013 年發表了利用 15 奈米厚度的矽薄膜作為 window 隔絕水溶液進而進行電化學實驗，但因軟 X 光光源並無法穿透此厚度的薄膜，因此他們利用大約 6 keV 的硬 X 光來做激發光源，透過計算如果具有 4.1 keV 動能的電子其 IMPF 的距離約為 7.5 nm，因此有 15% 的光電子訊號來自水溶液端因此可透過此方式獲得訊號。然而從 Photoionization cross section 來考量的話，高能量的激發光源，所得到的訊號強度並不會比較 X 光激發光源好，因此他們重新設計矽薄膜的厚度希望可以獲得更表面的訊息，目前可以成功將矽薄膜的厚度的降到 5 nm 的厚度，也利用了軟 X 光激發光源收集到部分訊號，雖說目前，並不能降到與 J. J. Velasco-Velez 所發表的利用石墨烯所製成的電化學 cell，但是未來其如果將厚度再減少其製作的方式將會遠比石墨烯容易，未來將具有很大的發展性，值得參考。



圖四: Takuya Masuda 教授所設計的電化學 cell。
(Appl. Phys. Lett. 2013, 103, 111605)

而來自 Shanghai Institute of Microsystem and Information Technology 的 Baohua Mao 博士，利用自行設計的固態電化學 cell(如圖五)，進行鈉氧電池的氧化還原反應，其裝置利用固態電解質使整個電化學 cell 可以直接置入近室壓 X 光光電子反應腔體裡，並在進電化學反應時也可以同時量測碳電極上的變化，可以清楚得知 Na_2CO_3 在電池

discharge 時會產生，而這些不導電物品的產生，使得跨過此電極的電壓有 potential loss 的現象，進而使能譜有一些往高束縛能位移。此固態電化學 cell 與我跟香港中文大學有點相似，相信未來可以將我們的電化學 cell 稍加修改也可以進行相似的實驗。



圖五.為 Baohua Mao 博士所設計的固態電化學 cell。

On the last day of the workshop (12/14), Hendrik Bluhm wrapped up the technical sessions with a last round table discussion on the issue of sample contamination, a seemingly trivial subject to non-practitioners. For UHV surface scientists, the contamination is not even an issue at all. However, for APXPS community, this cross contamination has become quite a common occurrence due to the permitted use of solvents, heated powder samples, and a large volume of gases in UHV chamber, with the problem exacerbated by the less frequent chamber bakeout. The chemicals used by previous users can linger in the chamber wall and become unexpected contaminants for later users. Bluhm summarized the findings in the following slide. Despite our relatively short experience in using APXPS (slightly more than one year), we already experienced some contamination problems mentioned in the slide and came up with various ways of combating this problem. We pay attention to the scheduling of

user experiments and bake the chamber if necessary to minimize the cross contamination. We also plan to implement the plasma cleaning, a more aggressive, extensive cleaning of the inside surfaces of the chamber. Hopefully, this problem can be brought under control.

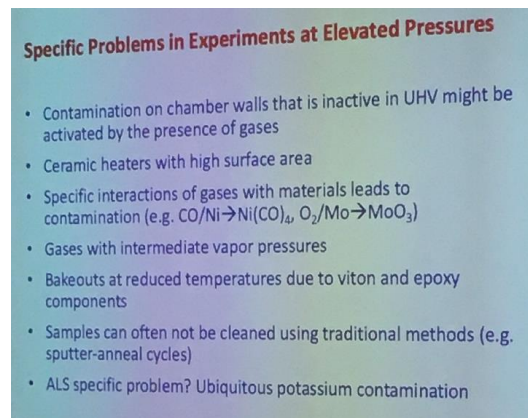


Figure 6. Bluhm summarized the findings of cross contamination in this slide.

除了演講之外，我在 poster section 時張貼了利用近室壓 X 光光電子能譜研究 TiOPc 分子感測 NO₂ 分子的機制，並且也與來自瑞典的學生 F. Rehman、英國的學生 Thokozile A. Kathyola 和德國博士後 J. J. Velasco- Velez 等人討論他們的實驗成果並分享自己對於他們實驗的看法。

建議事項：

感謝中心提供機會讓我出去參加此次會議，雖然近室壓 X 光光電子實驗站已於去年建立完成，但經過這一整年的運轉確實還有許多我們需要改善之處，能透過參與此種特別關注於特殊技術發展的會議是最快的學習方式。此次此會議在會前舉辦了有關技術分享的會議，對於管理實驗站與需要設計發展更新實驗站技術的我受益良多，期望中心能多支持實驗站管理人員參與此種會議以精進實驗站的技術，以便提供更好的設施給於用戶使用。