

Effect of Annealing Atmosphere on ZnGa₂O₄ : Mn²⁺ Thin Films

Z. X. CHEN¹, J. K. WU¹, Y. P. CHEN¹, B. Y. HUANG², H. Z. CHENG^{1*}

¹Department of Materials Science and Engineering, I-Shou University, Kaohsiung, Taiwan

²Department of Chemical Engineering, I-Shou University, Kaohsiung, Taiwan

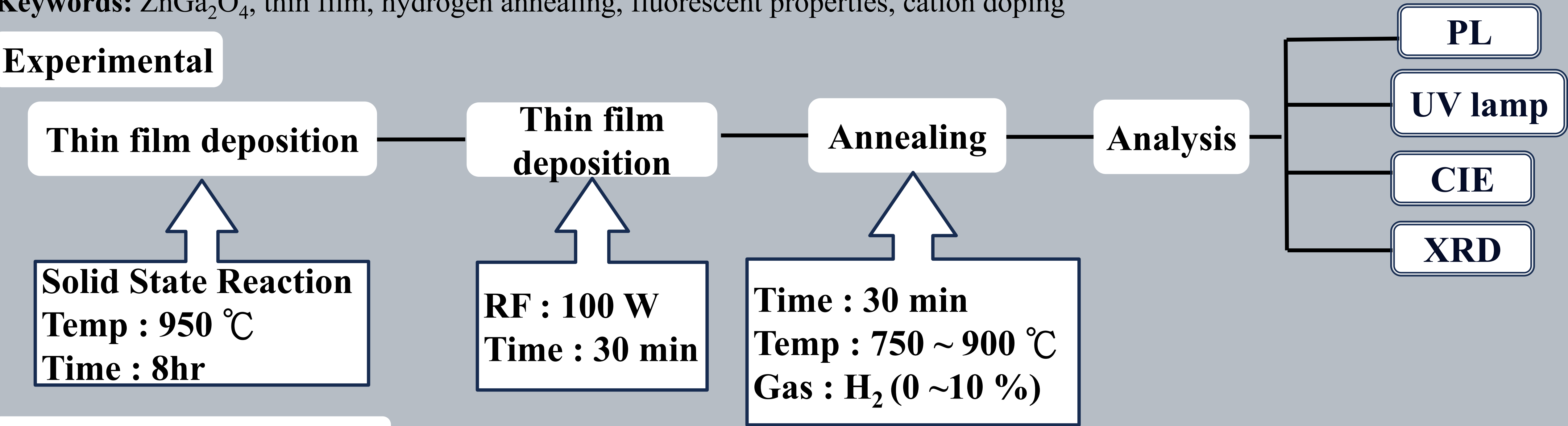
*E-mail: huyzu@isu.edu.tw

Abstract

In this experiment, we used ZnGa₂O₄ (ZGO) thin films doped with 0.5 wt% Mn²⁺. These films were annealed under various H₂ ratios and at different temperatures to analyze their photoluminescent properties. From the experimental results, as observed in Figure 1, the PL intensity decreases with a rise in temperature when the annealing temperature is at 750 °C. However, when the annealing temperature increases to 900 °C, the PL intensity is at its peak. When the annealing atmosphere is at 6% H₂/N₂, the PL intensity is at its strongest. Additionally, under UV light, the emitted brightness is also the highest. As the proportion of H₂ introduced increases, the PL intensity decreases. By altering the H₂ ratio and temperature, we can control the amount of inverse spinel structure.

Keywords: ZnGa₂O₄, thin film, hydrogen annealing, fluorescent properties, cation doping

Experimental



Results and Discussions

After annealing in different atmospheres, it was found that the fluorescence radiation intensity is the strongest under N₂. However, under O₂, the fluorescence radiation intensity decreases. It is speculated that it is oxidized during the preparation of the film, such as Figure 1. After subsequent annealing at different temperatures in an atmosphere of 5% H₂/N₂, it can be observed that the fluorescence radiation intensity will be stronger during annealing in H₂, confirming that there is oxidation during the preparation of the film, as shown in Figure 2, and finally changing the proportion of different H₂ ration. After annealing, it can be observed that the strongest fluorescence radiation intensity is at 6%. After XRD analysis and comparison with JCPDS Card, it can be observed that the (440) peak of ZGO appears during annealing in different atmospheres. It is speculated that the loss of Zn²⁺ leads to the formation of γ-Ga₂O₃ structure, as shown in Figure 4. With the temperature As the temperature rises, the intensity will decrease, as shown in Figure 5. After hydrogen annealing, the (311) peak of ZGO is more obvious, as shown in Figure 6. After CIE measurement, it can be found that the fluorescence saturation is the highest in the annealing atmosphere of 6% H₂/N₂, as shown in Figure 7.

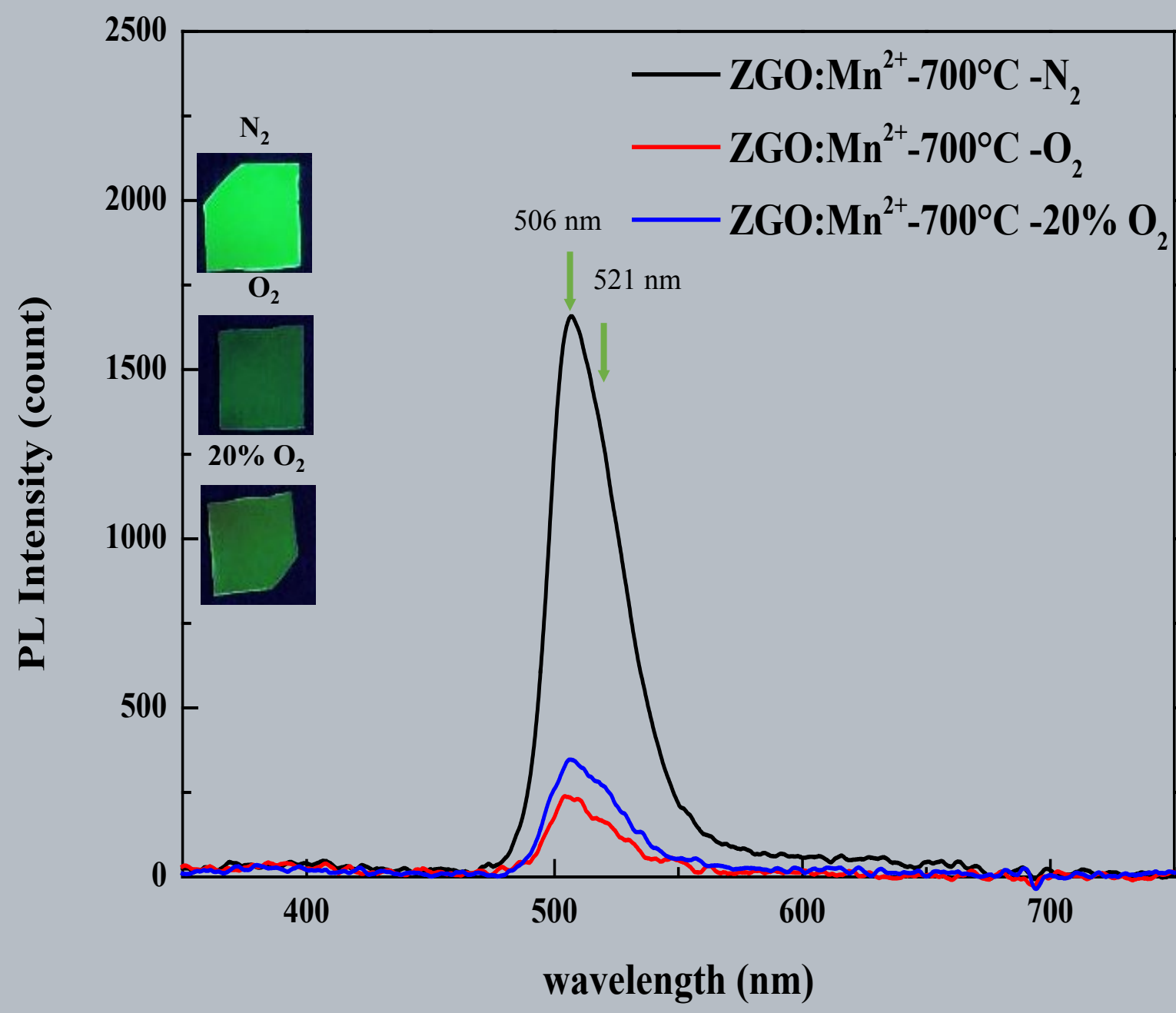


Figure 1. The PL and UV lamp irradiation images of Mn²⁺:ZGO films annealed under N₂, O₂, and 20% O₂ respectively.

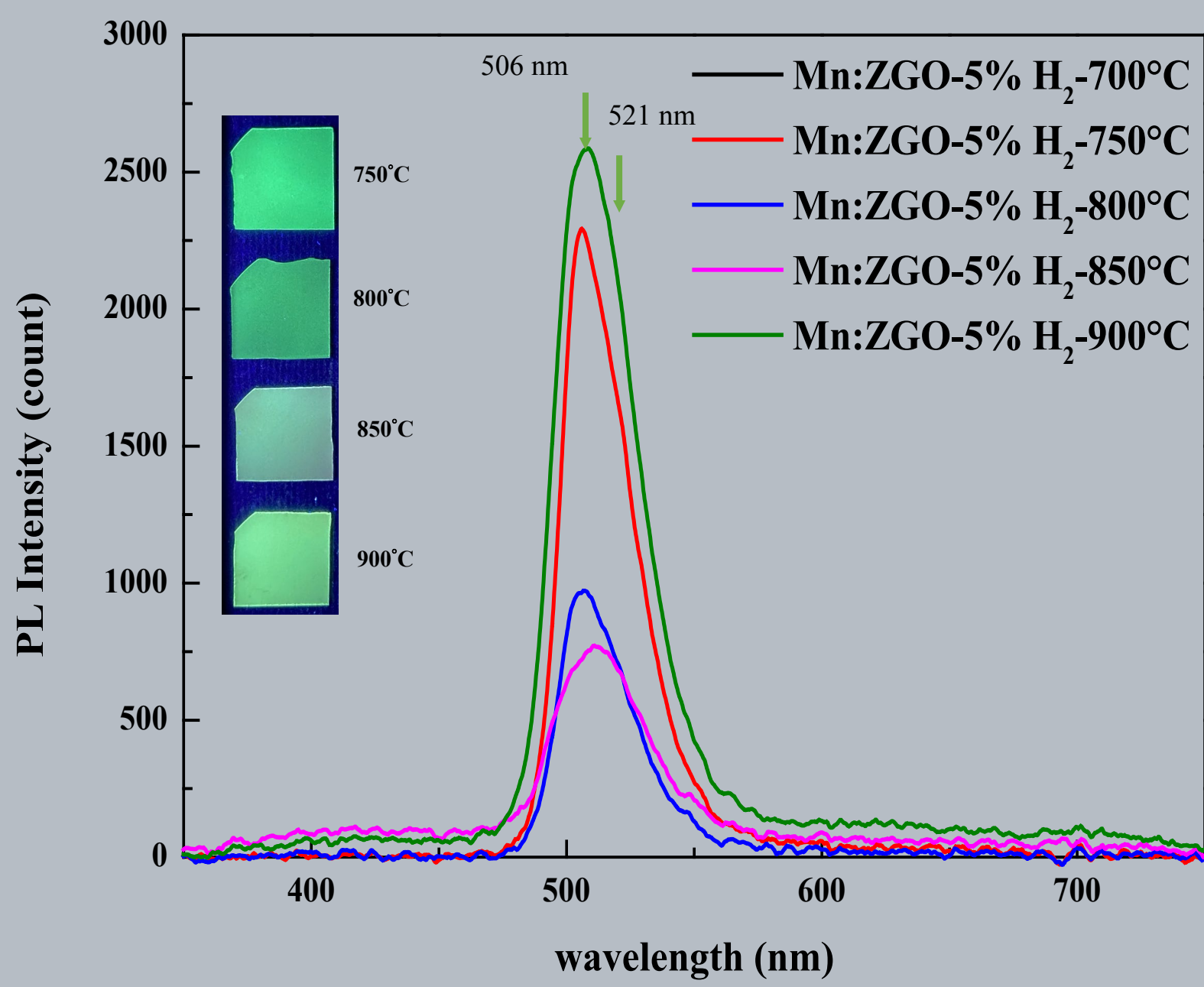


Figure 2. The PL and UV lamp irradiation images of Mn²⁺:ZGO films annealed at temperatures of 750 °C, 800 °C, 850 °C, and 900 °C in an atmosphere of 5% H₂/N₂.

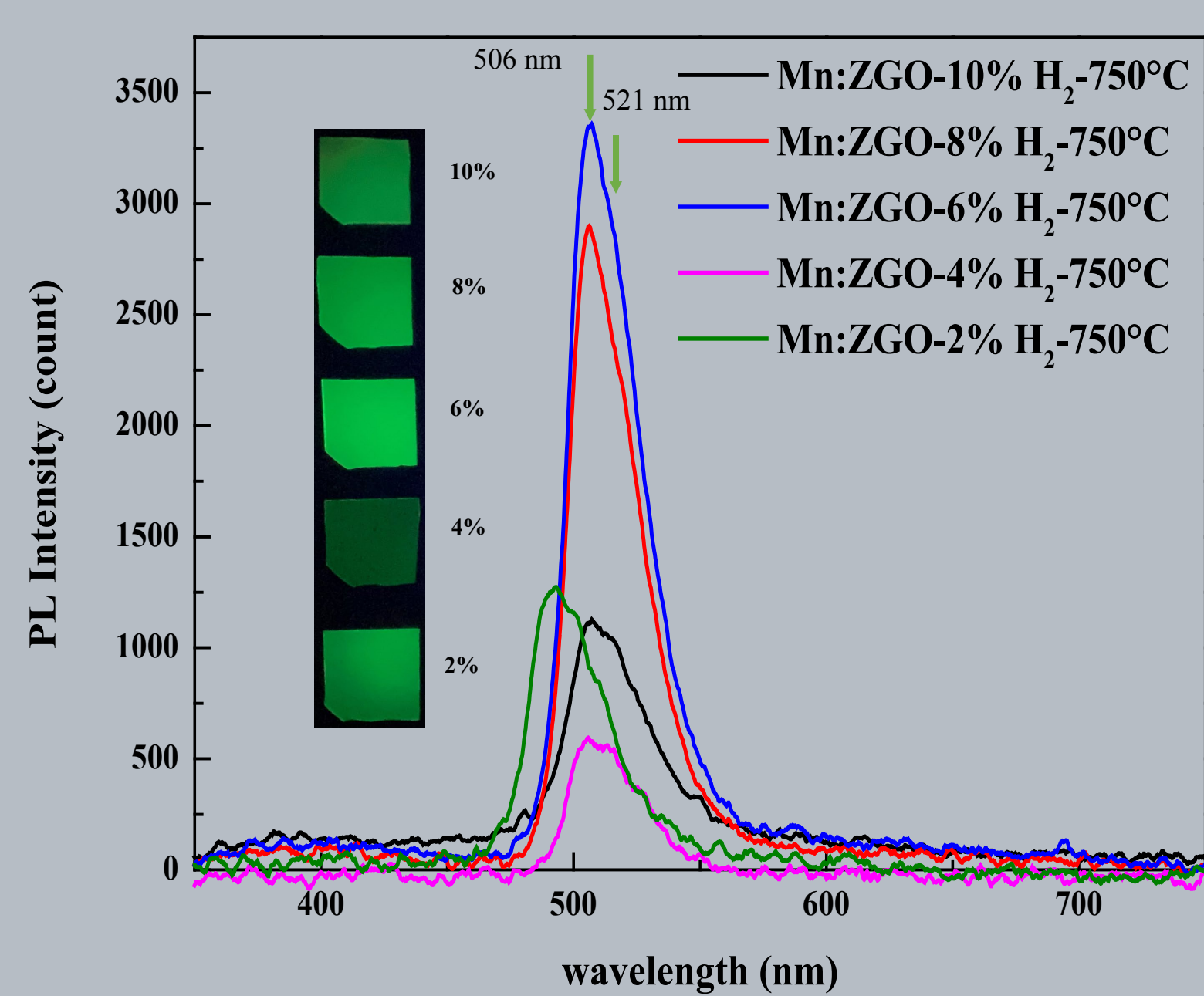
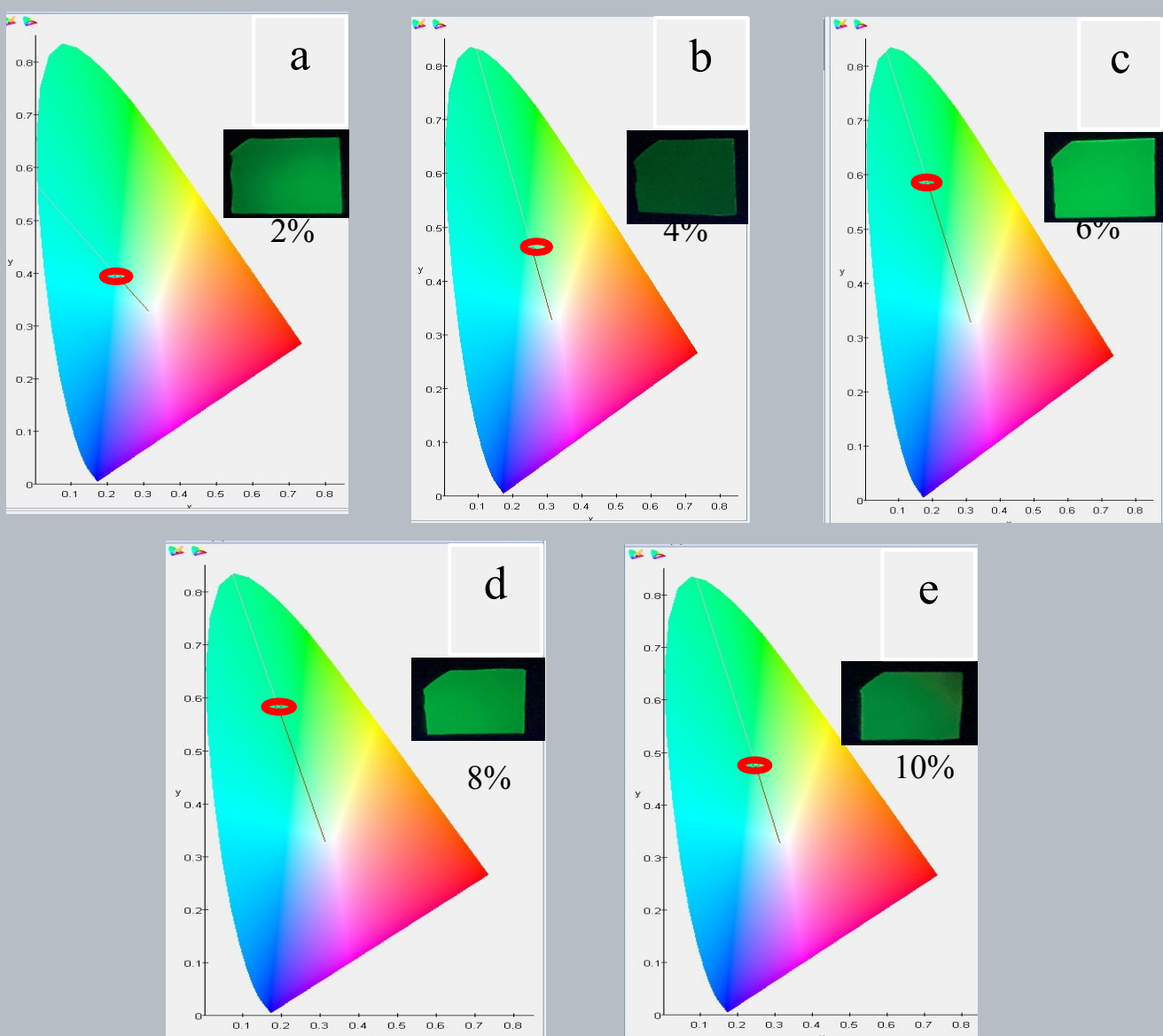


Figure 3. Mn²⁺:ZGO films annealed at H₂ ratios of 2% H₂/N₂, 4% H₂/N₂, 6% H₂/N₂, 8% H₂/N₂, and 10% H₂/N₂ at a temperature of 750 °C. PL and UV lamp irradiation diagram.



Figures 4. The CIE diagrams of Mn²⁺:ZGO annealed at (a) 2% H₂, (b) 4% H₂, (c) 6% H₂, (d) 8% H₂, and (e) 10% H₂.

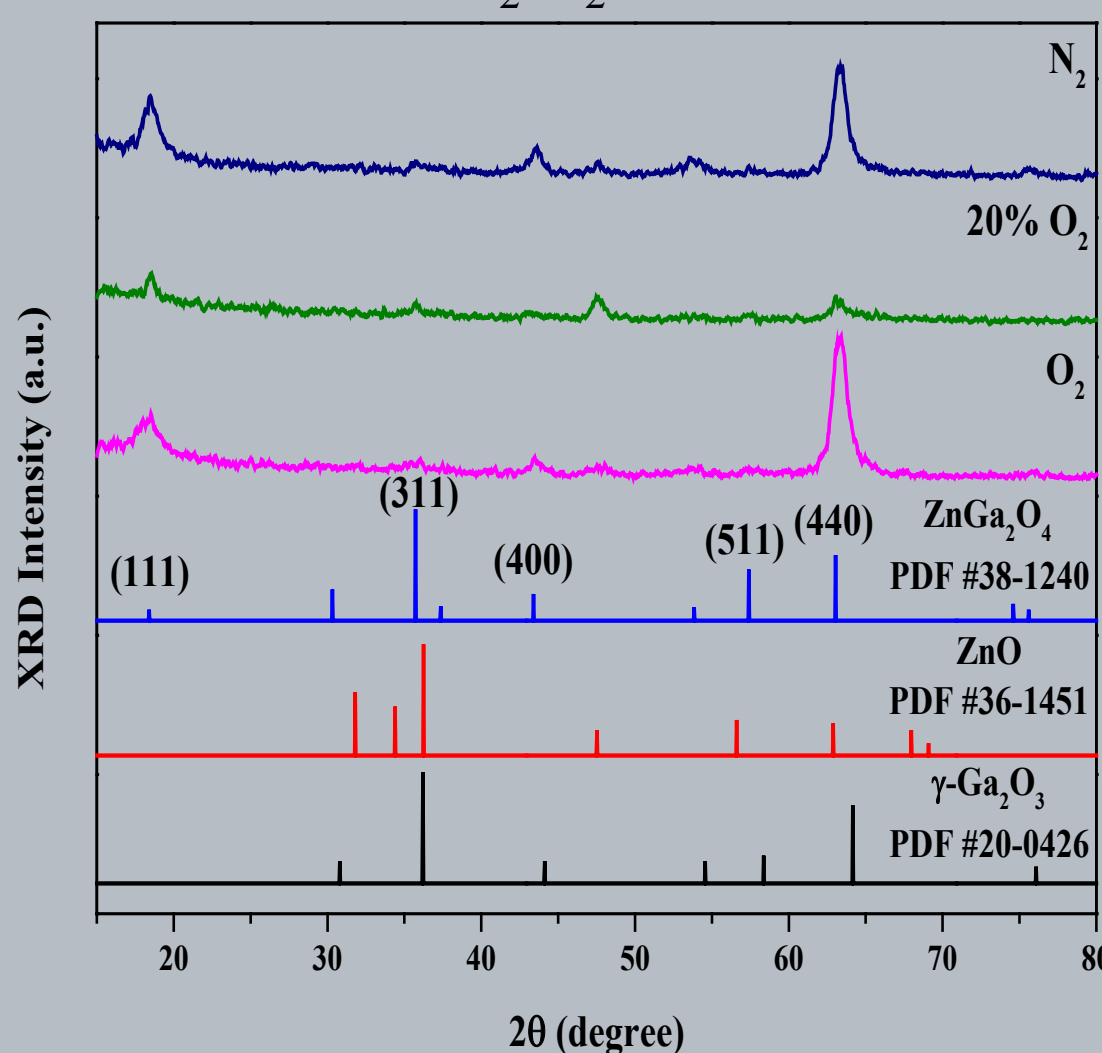


Figure 5. The XRD pattern after Mn²⁺:ZGO annealed under N₂, O₂, and 20% O₂ respectively.

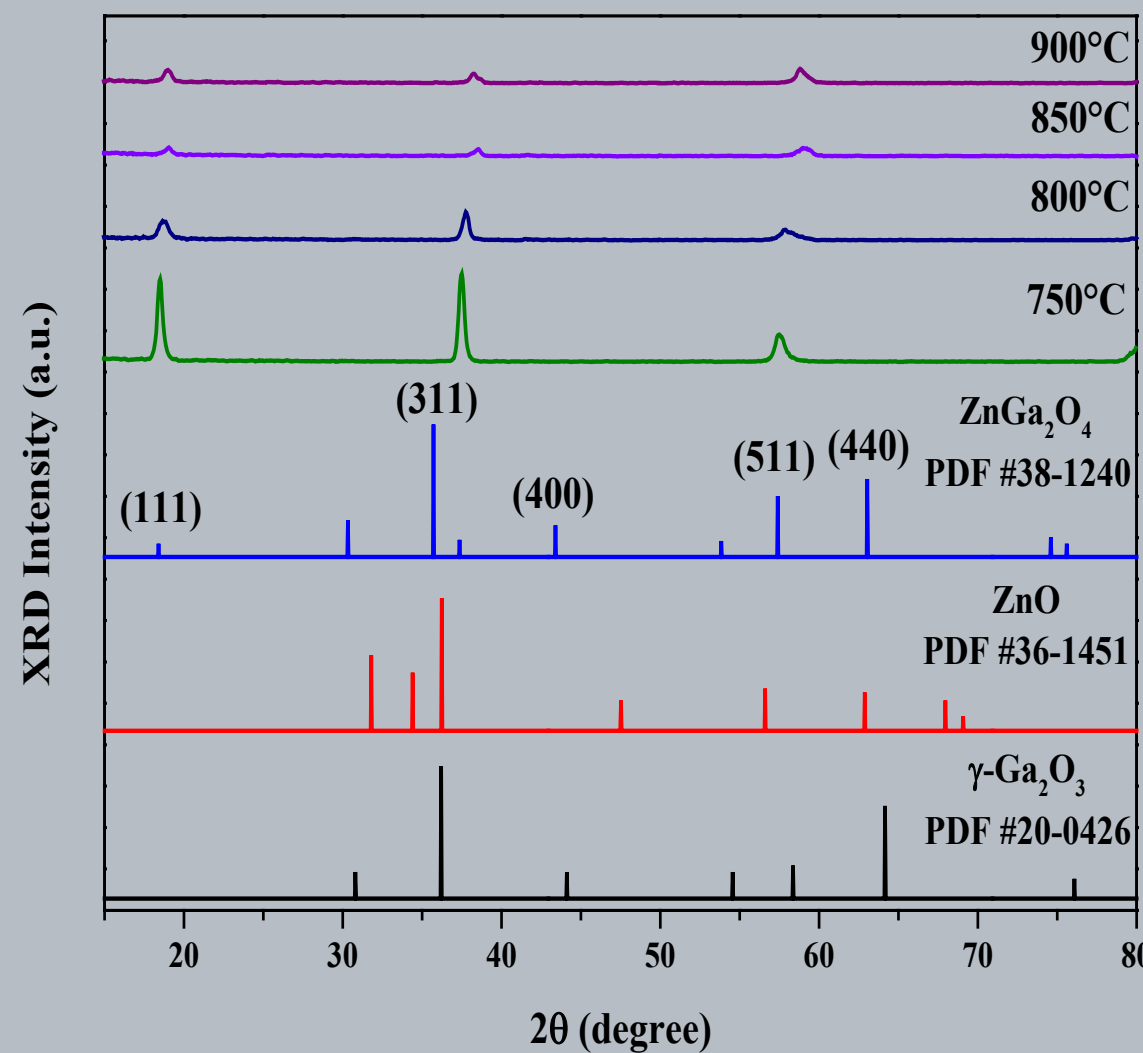


Figure 6. The XRD pattern after Mn²⁺:ZGO annealed at temperatures of 750 °C, 800 °C, 850 °C, and 900 °C in an atmosphere of 5% H₂/N₂.

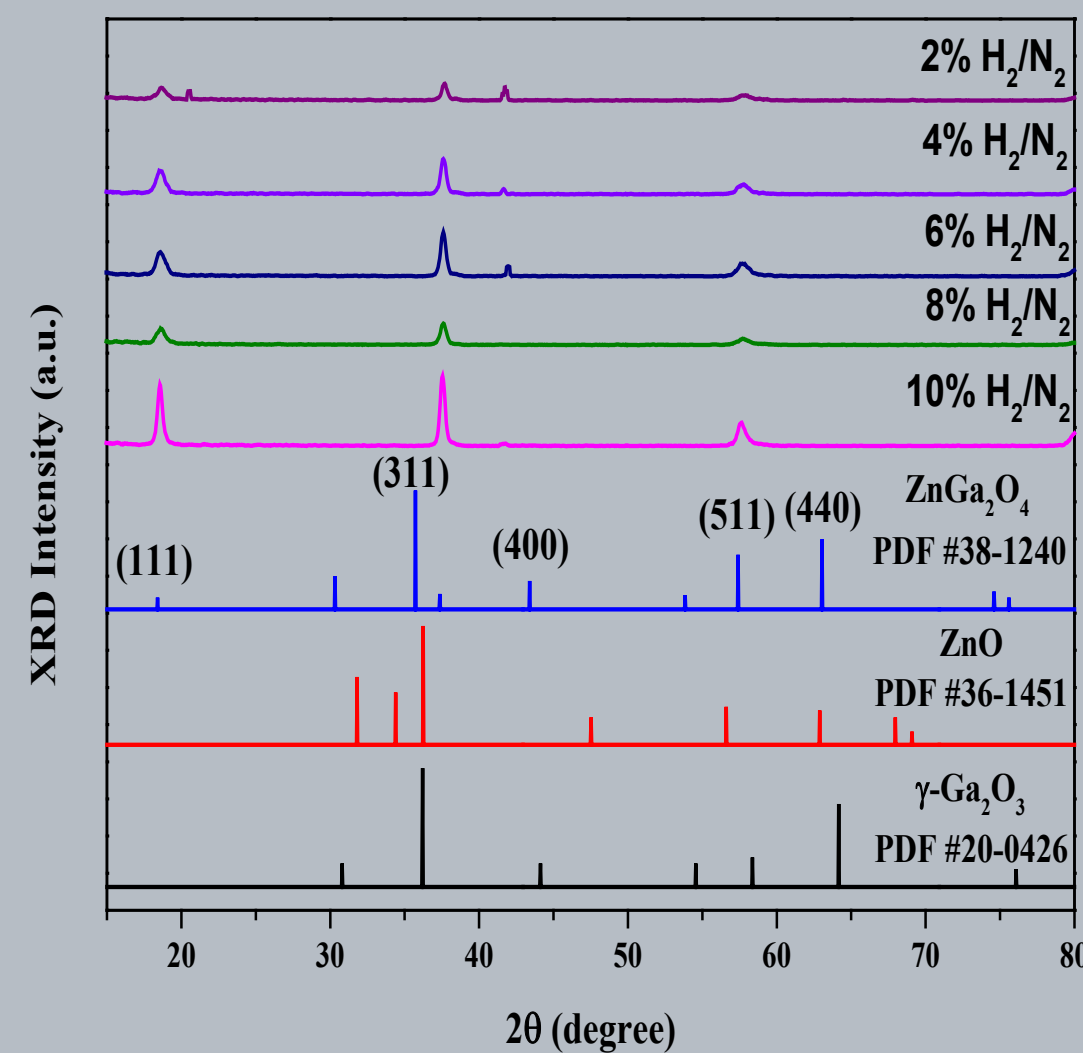


Figure 7. The XRD pattern after Mn²⁺:ZGO annealed at H₂ ratios of 2% H₂/N₂, 4% H₂/N₂, 6% H₂/N₂, 8% H₂/N₂, and 10% H₂/N₂ at a temperature of 750 °C. PL and UV lamp irradiation diagram.

Conclusion

1. Annealing in the environment of N₂, O₂ and 20 % O₂, N₂ has the strongest fluorescence radiation intensity and brightness, and can be used as a protective atmosphere to prevent Mn²⁺ from oxidizing into Mn³⁺.
2. Annealing at different temperatures of 5% H₂/N₂. At high temperatures, the oxidation ability will increase, causing the loss of Zn²⁺.
3. Annealing under different ratios of H₂/N₂, 6% H₂/N₂ has the strongest fluorescence radiation intensity and brightness. As the H₂/N₂ ratio increases, the luminescence reaction will be changed due to concentration quenching.
4. After annealing by H₂, the fluorescence radiation intensity increases, confirming that the film has a tendency to oxidize when preparing the film.

Acknowledgement

The authors are grateful to MOST for the financial support of this study under the Contract NO : MOST110-2221-E-214-016 & MOST108-2635-E-214-00

鎳摻雜鋇鐵氧化物鈣鈦礦結構 超級電容電極之研究

林維詩 *林炯棟 鄭君皓 劉晏廷 洪國維

摘要

在現今這個能源枯竭的時代，環保逐漸意識抬頭，而超級電容為一種高功率、高能量、具良好循環壽命等優點的能量儲存裝置。本研究利用 Pechini 法製備鋇鐵鎳氧化物，由於鈣鈦礦結構氧化物 (ABO_3) 具較佳的導電性與電化學性，藉由改變 B 位元素的摻雜量，提高結構的氧空位數量，並探討不同煅燒溫度對其特性與影響，再利用 SEM、XRD、循環伏安及交流阻抗對此電極材料進行分析。

實驗步驟

粉末製備

依化學劑量表秤重後加入水與酒精(1:1)均勻混合

加入檸檬酸做為螯合劑

加入乙二醇使其發生酯化反應

利用 IR 燈將混合溶液烤乾並研磨

進行以 $3^\circ\text{C}/\text{min}$ 的升溫速率及持溫 2 小時煅燒

電極製備

裁剪並清洗泡沫鎳基板

待測粉體、PVDF、Super P 以 80:10:10 的比例混合

塗佈在泡沫鎳基板上

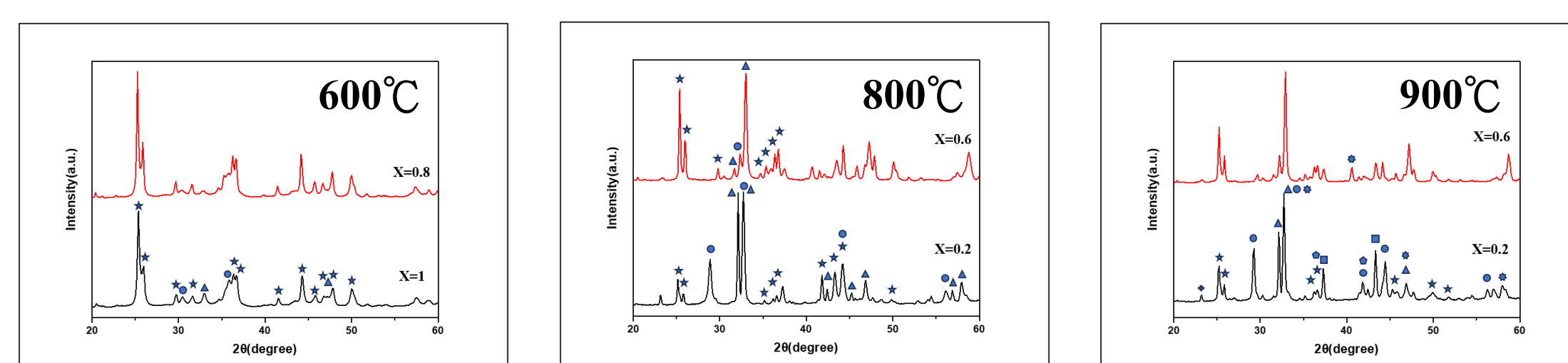
烘乾

電化學分析

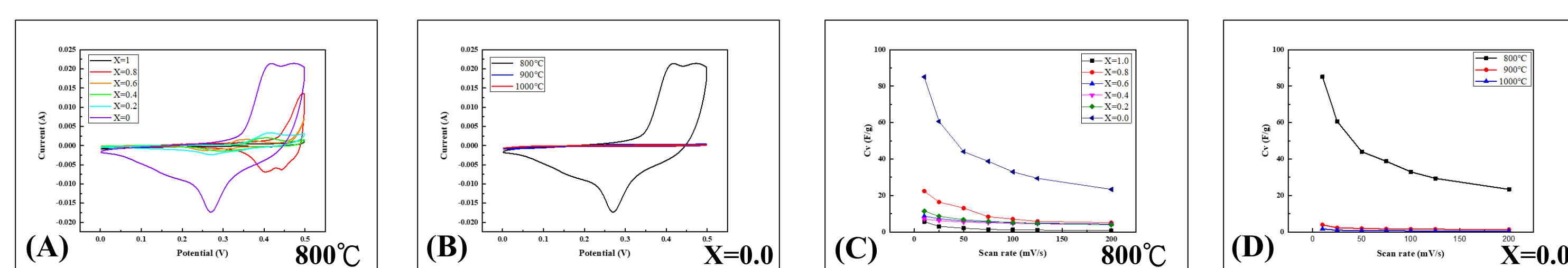
結果與討論



XRD 分析

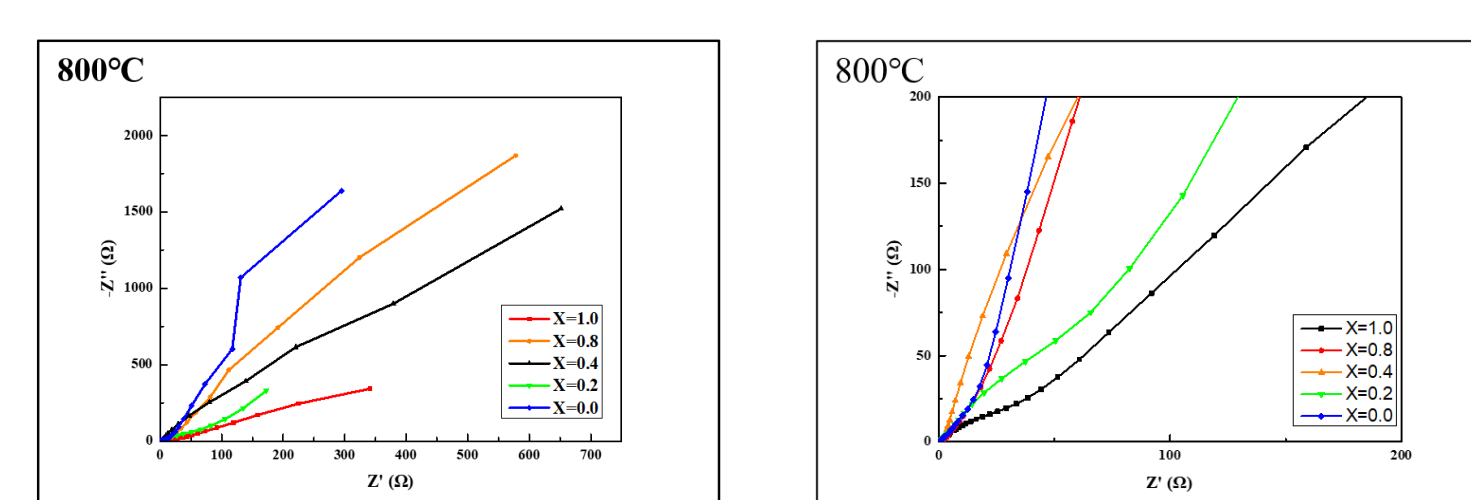


循環伏安分析

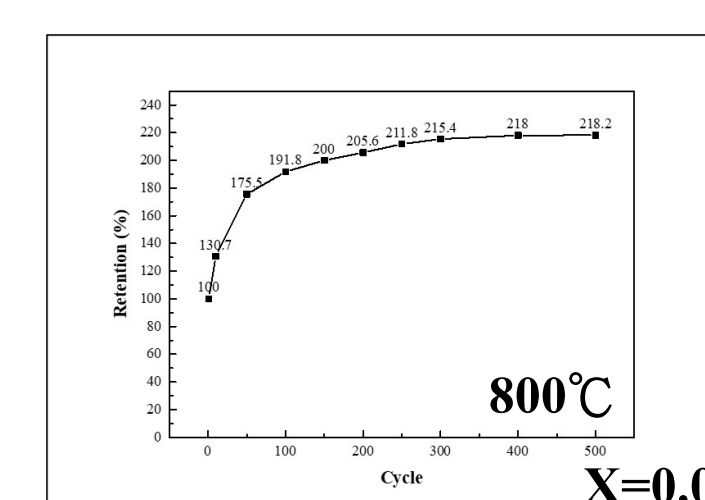


(A)不同比例掃描速率10mV/s、(B)不同比例之比電容值、
(C)不同溫度掃描速率10mV/s、(D)不同溫度之比電容值

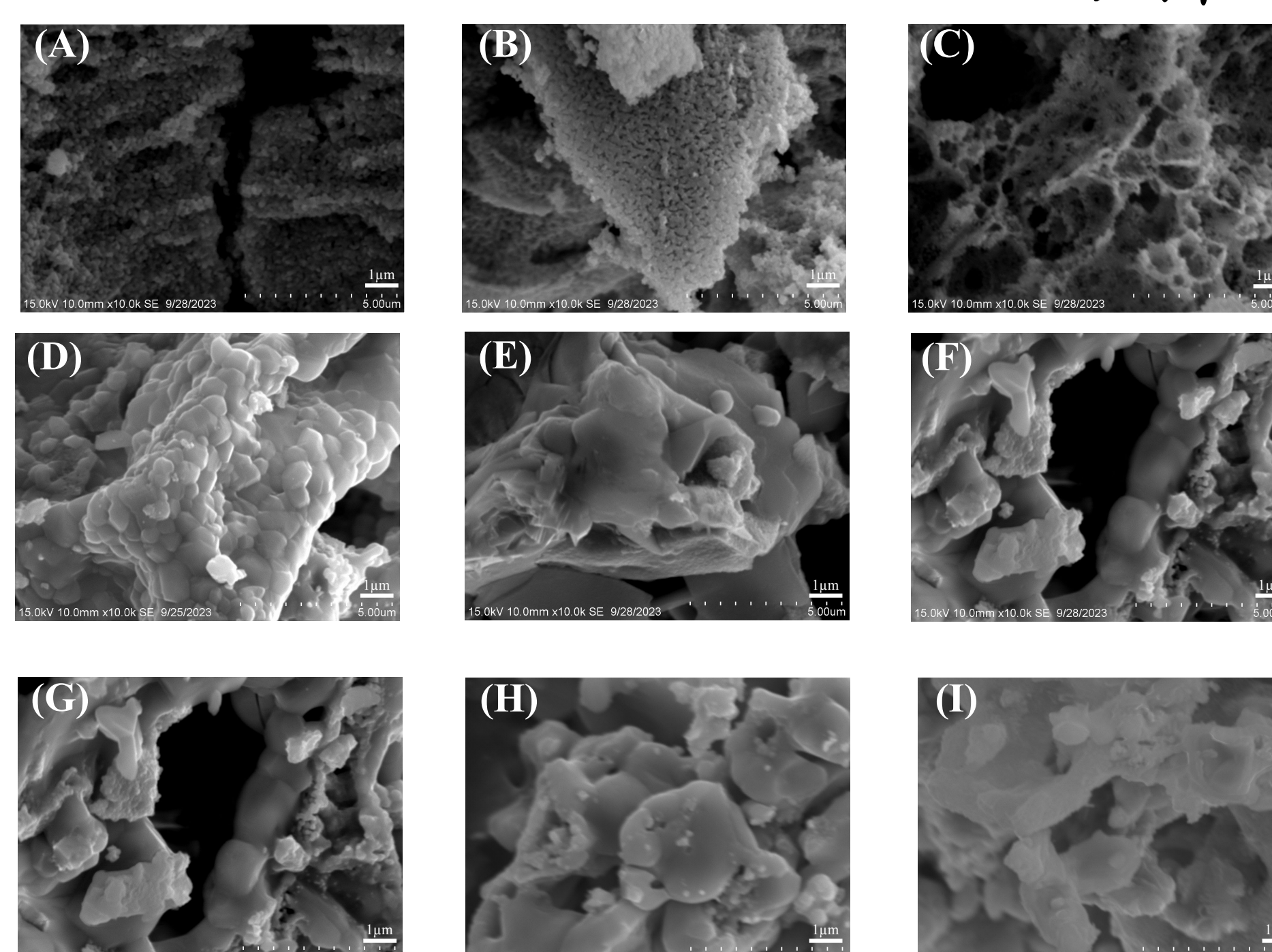
交流阻抗分析



循環壽命分析



SEM 分析



800°C (10000X)
(A) SrFeO_3
(B) $\text{SrFe}_{0.8}\text{Ni}_{0.2}\text{O}_3$
(C) $\text{SrFe}_{0.6}\text{Ni}_{0.4}\text{O}_3$
(D) $\text{SrFe}_{0.4}\text{Ni}_{0.6}\text{O}_3$
(E) $\text{SrFe}_{0.2}\text{Ni}_{0.8}\text{O}_3$
(F) SrNiO_3

SrNiO_3 (10000X)
(G) 800°C、
(H) 900°C、
(I) 1000°C

結論

- 隨著鎳含量的增加，結構表面出現孔洞且一次粒子增大，有助於提高材料表面積。
- 隨著溫度的上升， SrCO_3 相有減少的趨勢，且 $\text{SrFe}_x\text{Ni}_{1-x}\text{O}_3$ 相也隨之增加。
- 由氧化還原峰得知，當鐵和鎳的比例為 0:1 實據有最佳的比電容值 85.07 F/g。
- 由交流阻抗圖中，斜率越大且 R_{CT} 值越小者，其比電容值越高。
- SrNiO_3 在 800°C 時的循環壽命由 100% 升至 218.2%，由後期的比電容維持常數可知此材料具有高穩定性。

Effects of High-Power LASER Parameters and Simplified Heat Treatment Processes on the Repair Welding Characteristics of the Precipitation-Strengthened Copper Alloys

P.Y. Huang, H.S. Wang*, H.G. Chen, Y.T. Tong, and Y.S. Lai

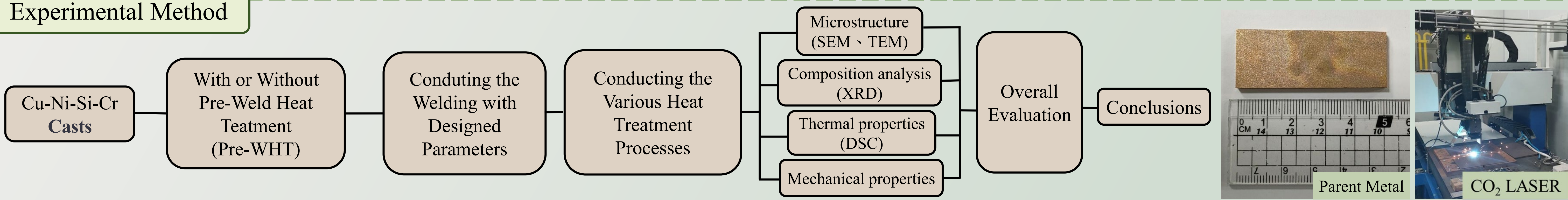
Department of Materials Science and Engineering, I-Shou University, Kaohsiung, Taiwan.

*E-mail:huei@isu.edu.tw

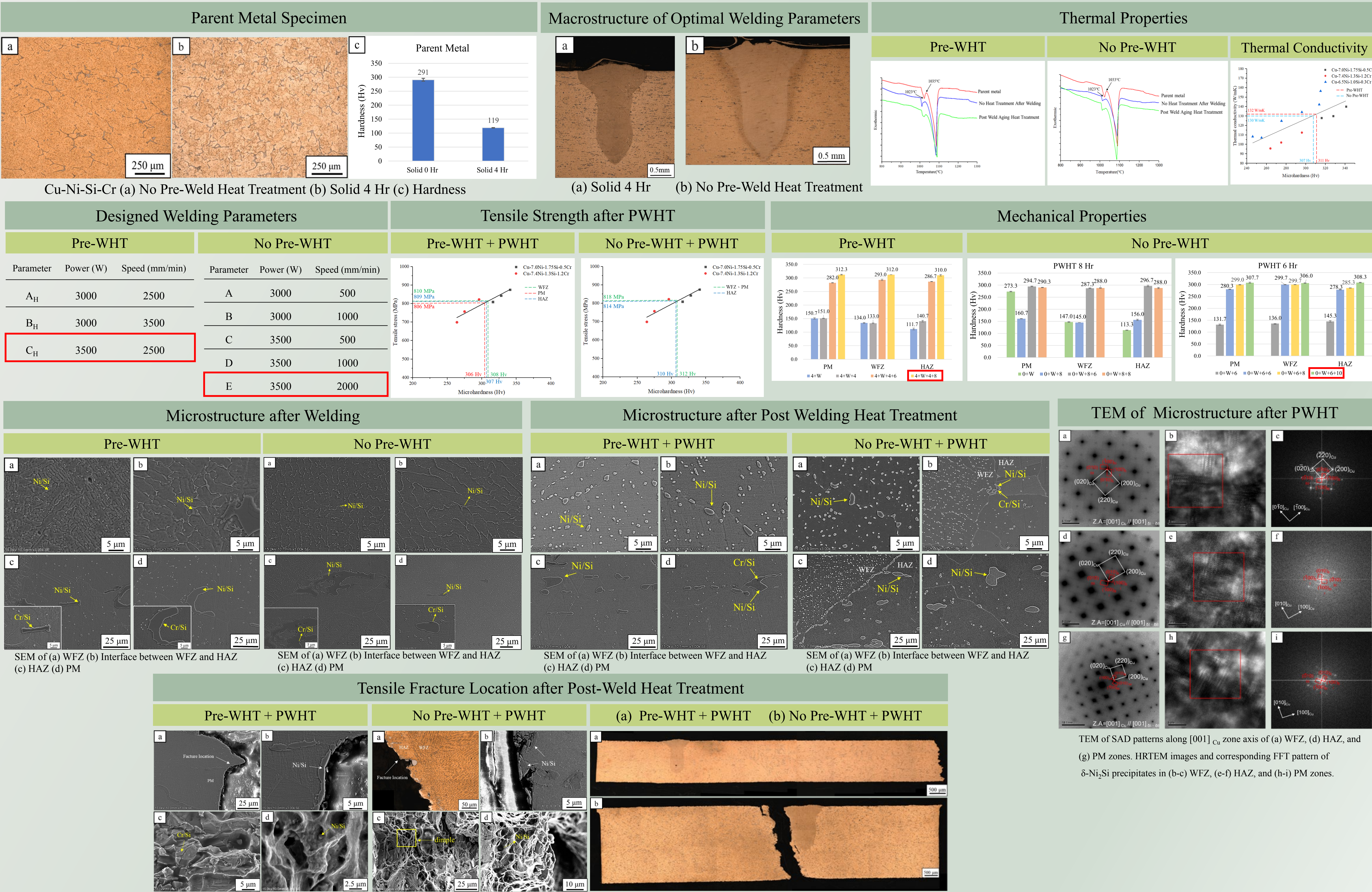
Abstract

- To investigate the effects of the high-power LASER technology on the repair welding characteristics of a novel high-strength and high-thermal conductivity copper alloy casts (Cu-7.0Ni-1.75Si-0.5Cr).
- This study uses a simplified repair welding process, exempting pre-weld heat treatment and preheating, by using CO₂ LASER technology. Then, All welded samples are post-weld heat treated (PWHT).
- Microstructure observations,mechanical and thermal properties evaluation of the welds are conducted,to understand the feasibility of the simplified repair welding processes.

Experimental Method



Results and Discussion



Conclusions

- This study providing the designed welding parameters and post weld heat treatment for the simplified CO₂ LASER repair welding process for the new high-strength copper alloy castings.
- This study offers a simplified CO₂ LASER repair welding process for the new high-strength copper alloy with good quality and establish its correlation with microstructure, thermal properties, and mechanical properties.
- This project offers the new high-strength copper a repair solution that can significantly reduce the cost losses associated with the disposal of defective molds.
- The simplified CO₂ LASER repair welding process designed in this study reduces the energy requirements for the heat treatment processes.

Acknowledgments

We thank the National Science and Technology Council ,for financial support (MOST 111-2813-C-214-010-E) at ISU for experimental assistance .

以導熱性陶瓷取代銅原料製作無銅環保磨擦材料

陳昱綸、黃宣嘉、曾聖淮、張立廷、劉柏駒、李虹霓、羅顯宸、楊智凱
指導教授：李國榮 教授 義守大學 材料科學與工程學系

研究動機及目的

目前商用磨擦材料大多為非石棉有機磨擦材料(Non-Asbestos Organic friction material, NAO)，具有成本低、噪音小、穩定的磨擦係數(0.2-0.6)、材料取得容易...等優點。其中，**銅原料**(銅粉、銅纖維)是不可或缺的成分之一，因為它提供許多功能特性，如結構完整性、高導熱及散熱性、高延展性和高溫下良好的潤滑性。但近期研究指出，**銅磨損後的碎屑將導致水生生物快速死亡**，進而危及整個水生生態，因此美國環境保護署要求在2025年時，將煞車材料中的銅含量降低到0.5 wt%以下。

因此，本研究以**高硬度**、**高耐磨**及**高導熱性**之陶瓷原料(**氮化硼**、**碳化矽**、**氮化鋁**及**氮化矽**)作為銅原料的取代材，製作導熱性陶瓷無銅磨擦材料，探討各試片在機械、熱傳導、磨潤性質等方面的表現，並評估其應用在煞車系統中的可行性。



煞車系統



來令片



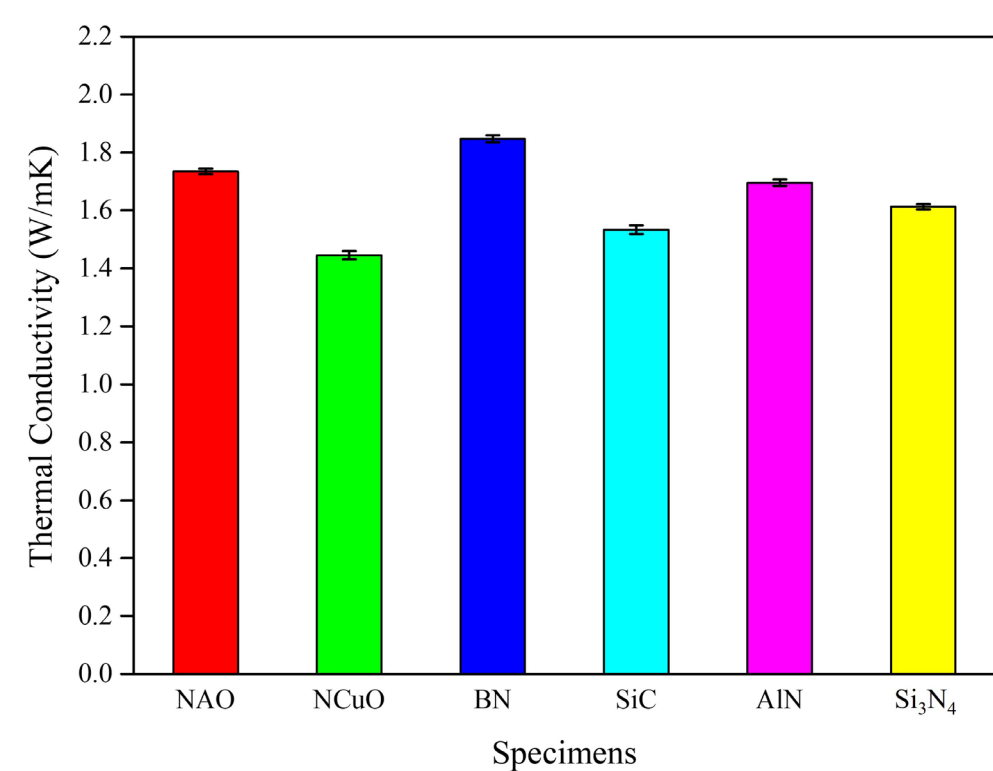
陶瓷粉末

實驗方法

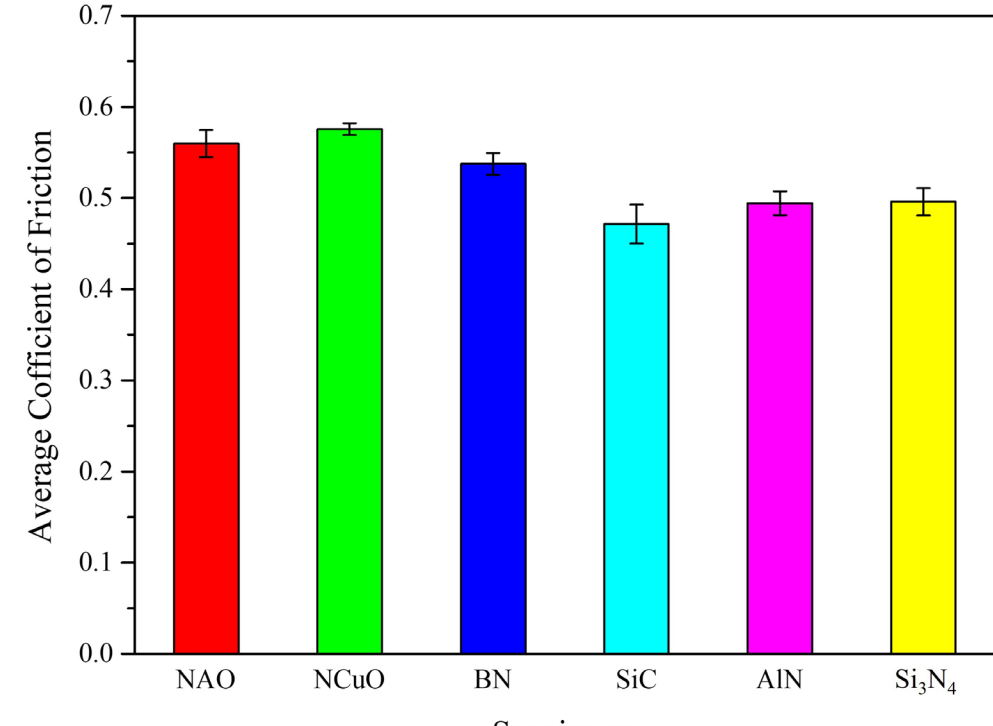
各類試片代號及成分表(單位: vol%)

代號	成分	銅粉/ 銅纖維	氮化硼	碳化矽	氮化鋁	氮化矽	其他
對照組	NAO	5.1	-	-	-	-	94.9
	NCuO	-	-	-	-	-	100
實驗組	BN	-	5.1	-	-	-	94.9
	SiC	-	-	5.1	-	-	94.9
	AlN	-	-	-	5.1	-	94.9
	Si ₃ N ₄	-	-	-	-	5.1	94.9

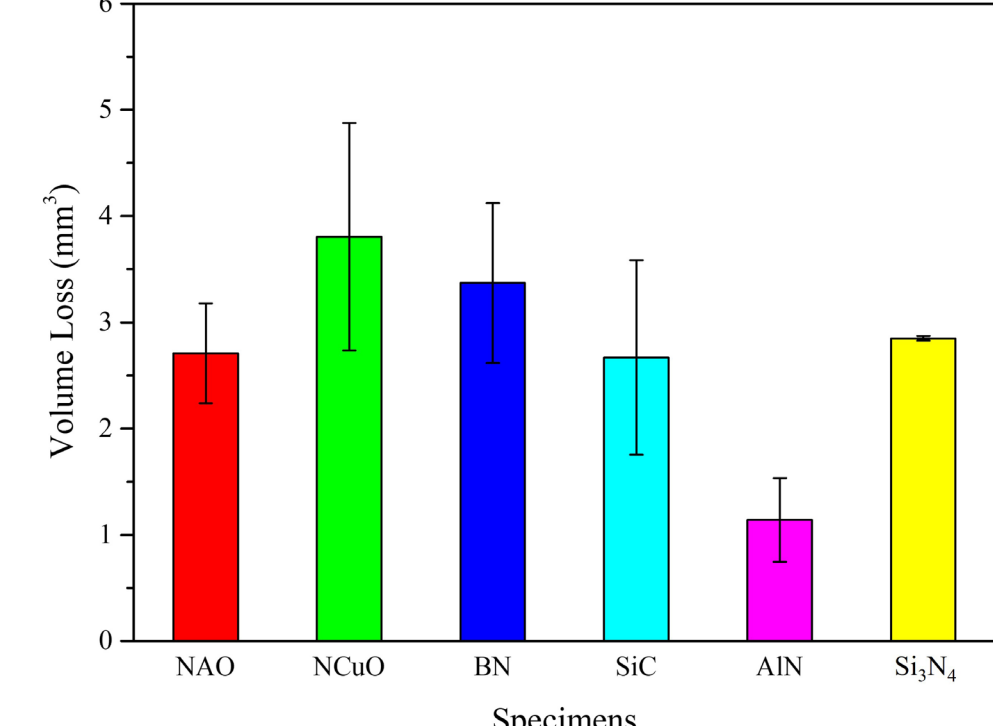
※其他：酚醛樹脂、芳綸纖維、鈦酸鉀纖維、銅絲絨、二氧化鋯、二氧化矽、腰果殼油顆粒、鋁粉、石墨、硫酸鋇、碳化矽、硫化錒及NBR等。



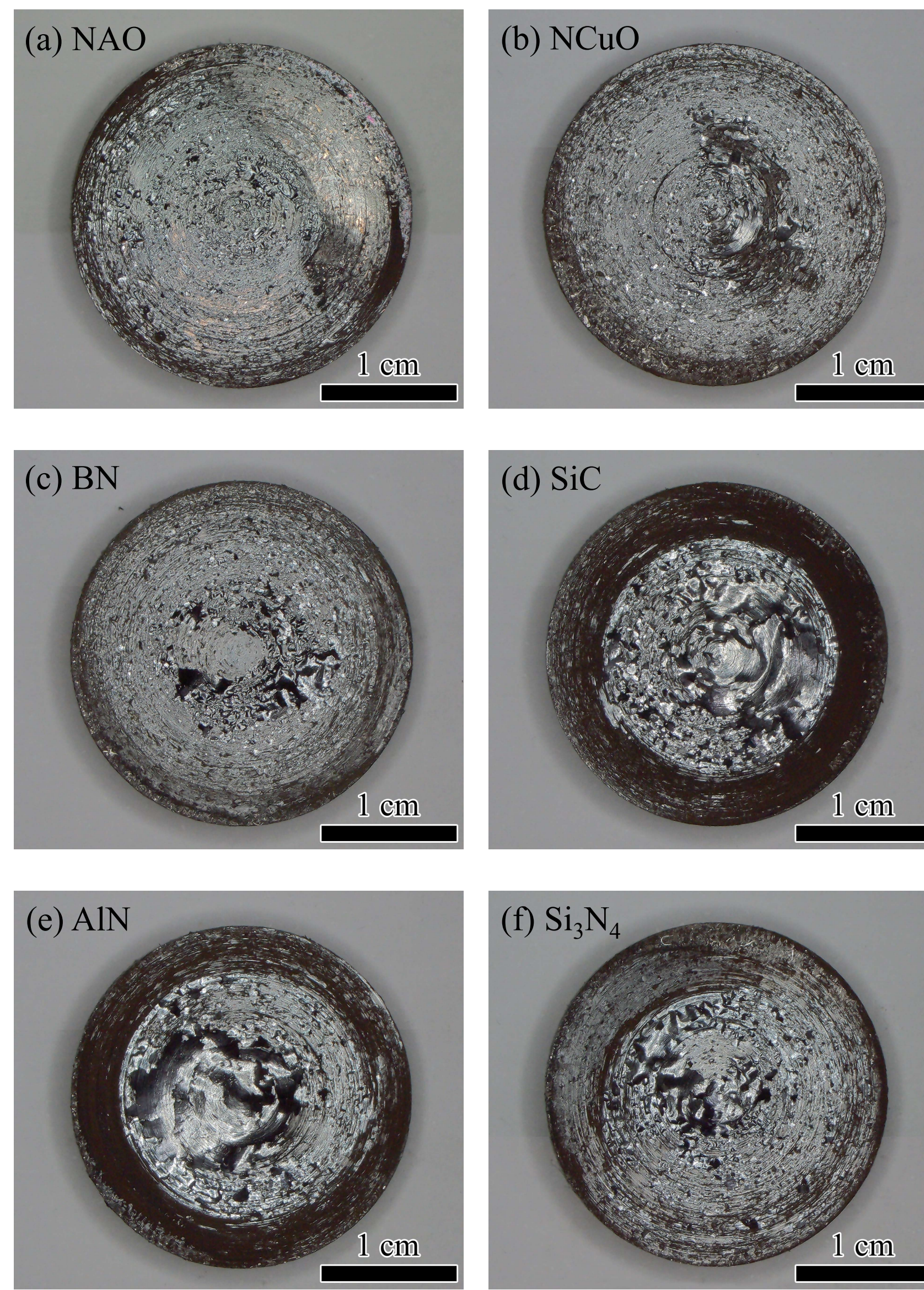
各類試片之熱傳導係數



各類試片之平均磨擦係數



各類試片之磨耗量



各類試片磨耗後顯微結構圖

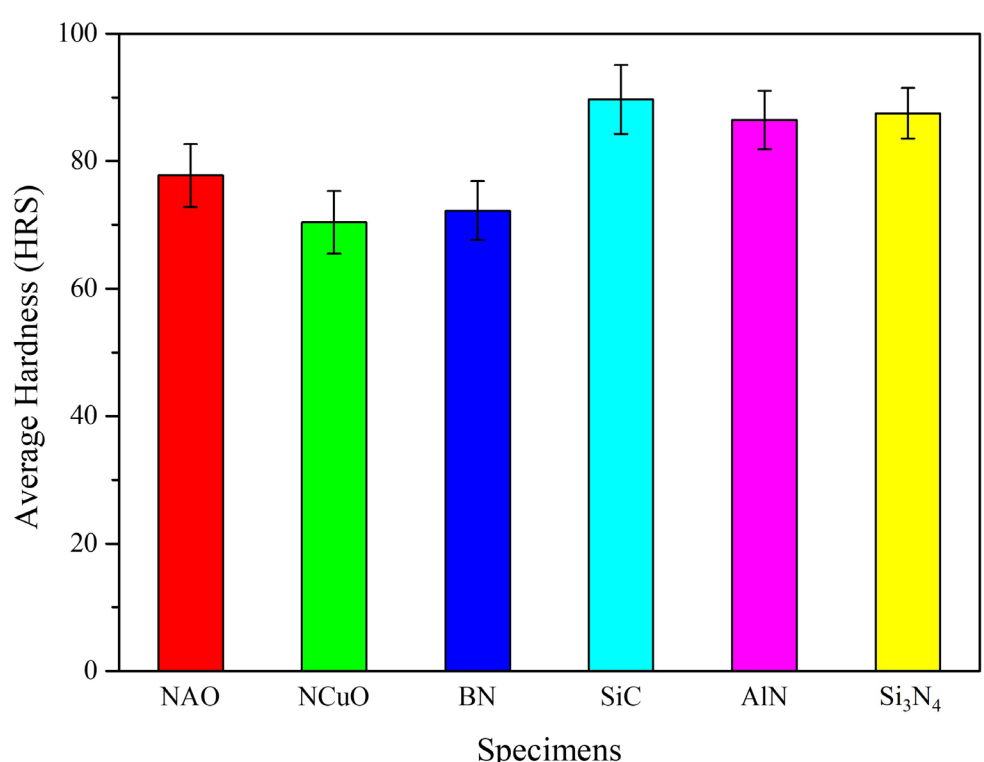
結論

- 從機械性質分析及熱傳導測試中可以發現，添加各類陶瓷粉末取代銅原料的試片之硬度、抗彎強度和熱傳導係數皆明顯大於無銅NCuO試片，此說明**氮化硼、碳化矽、氮化鋁和氮化矽**的添加，有助於增加無銅磨擦材料的導熱性和機械性質。
- 在磨耗試驗中可以觀察到，經模擬煞車磨耗後，試片表面之磨潤層面積越大且有明顯磨屑堆積者，磨擦係數越低，磨耗量越小，粗糙度越大；磨潤層面積越小且有面積平整的磨擦層者，磨擦係數越高，粗糙度越小；而較無磨潤層且磨潤層易剝落者，磨耗量較大。
- 綜合各類試片在硬度、抗彎強度、熱傳導性質、磨擦係數及磨耗量(體積損失)等方面的表現進行評估，發現**利用氮化鋁(AlN)及碳化矽(SiC)較具潛力取代銅原料製作無銅環保磨擦材料**。

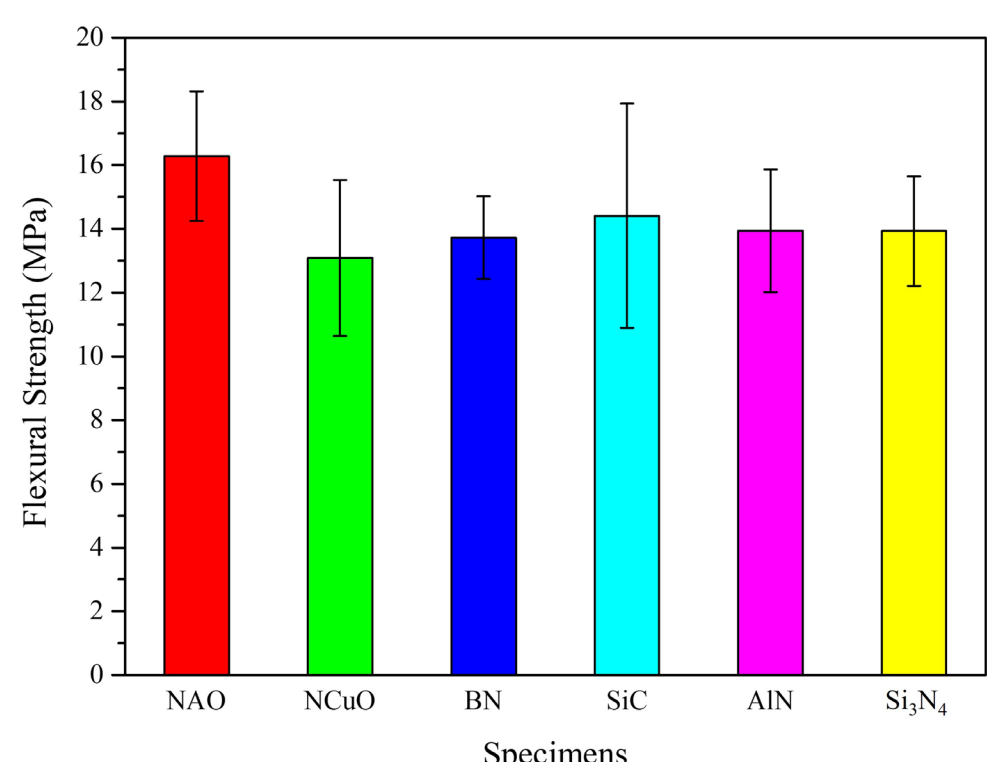
致謝

由衷感謝義守大學貴儀中心提供量測設備與儀器及大詠城機械提供原料(鑄鐵)，使本研究順利進行各項實驗，僅此致謝。

結果與討論



各類試片之平均硬度



各類試片之抗彎強度

以自製多孔碳微球改質美耐皿海綿用於海洋溢油吸附技術之研究

陳珮瑄、陳宣友、薛家鈺、徐悠、陳意、陳仲信、紀祉伊、吳翊瑄、洪宥翔

指導教授：李國榮 教授
義守大學 材料科學與工程學系

摘要

海洋中油輪原油的洩漏污染層出不窮，因此開發具低成本、多功能性且重複使用性高的油/水分離材料相當重要。本研究採用自製的**木糖基多孔碳微球**混合具有**疏水性**和**穩定性的聚二甲基矽氧烷** (Polydimethylsiloxane, PDMS)製成改質劑，並製備相同改質劑量的商業奈米碳管、石墨烯及活性炭改性海綿進行比較，先初步比較篩選出改質後疏水效果較佳的碳基材料，並進行後續一連串的親/疏水性質及油水分離測試。實驗結果顯示，自製的多孔碳微球試片水滴接觸角相較於奈米碳管、石墨烯及活性炭試片大，其中又以0.6 g的自製碳微球試片水滴接觸角高達 159.28° ，**疏水性能最佳**。經一連串實驗證實，自製多孔碳微球改質試片於溫度、曝曬/暴露、海水搖晃及連續壓縮測試下，接觸角(疏水性)皆無明顯變化，**環境適應能力佳**。自製多孔碳微球改質試片透過真空抽氣裝置可**快速連續油水分離**。

關鍵字：油/水分離、超疏水、多孔碳微球、奈米碳管、石墨烯、活性炭

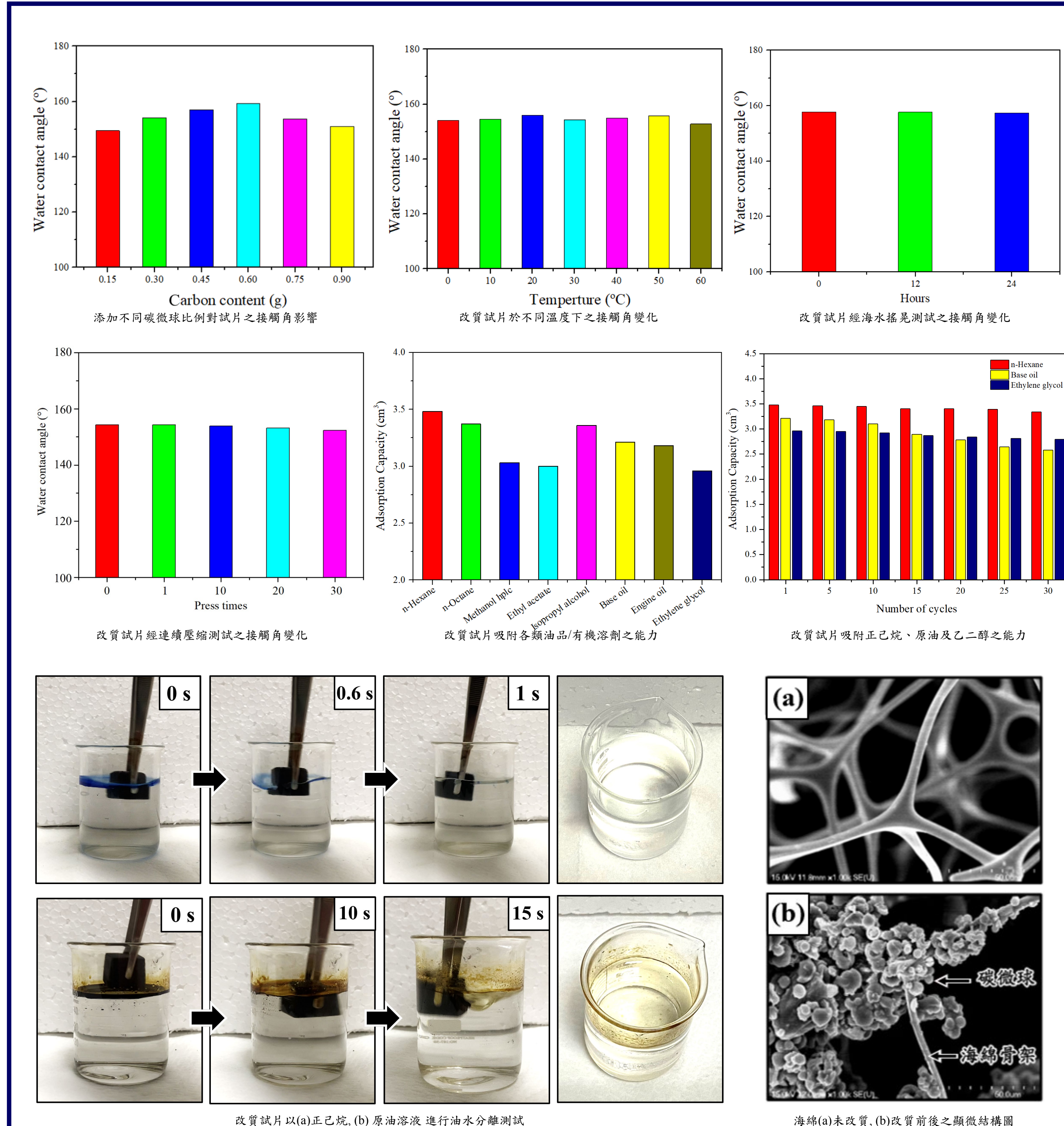
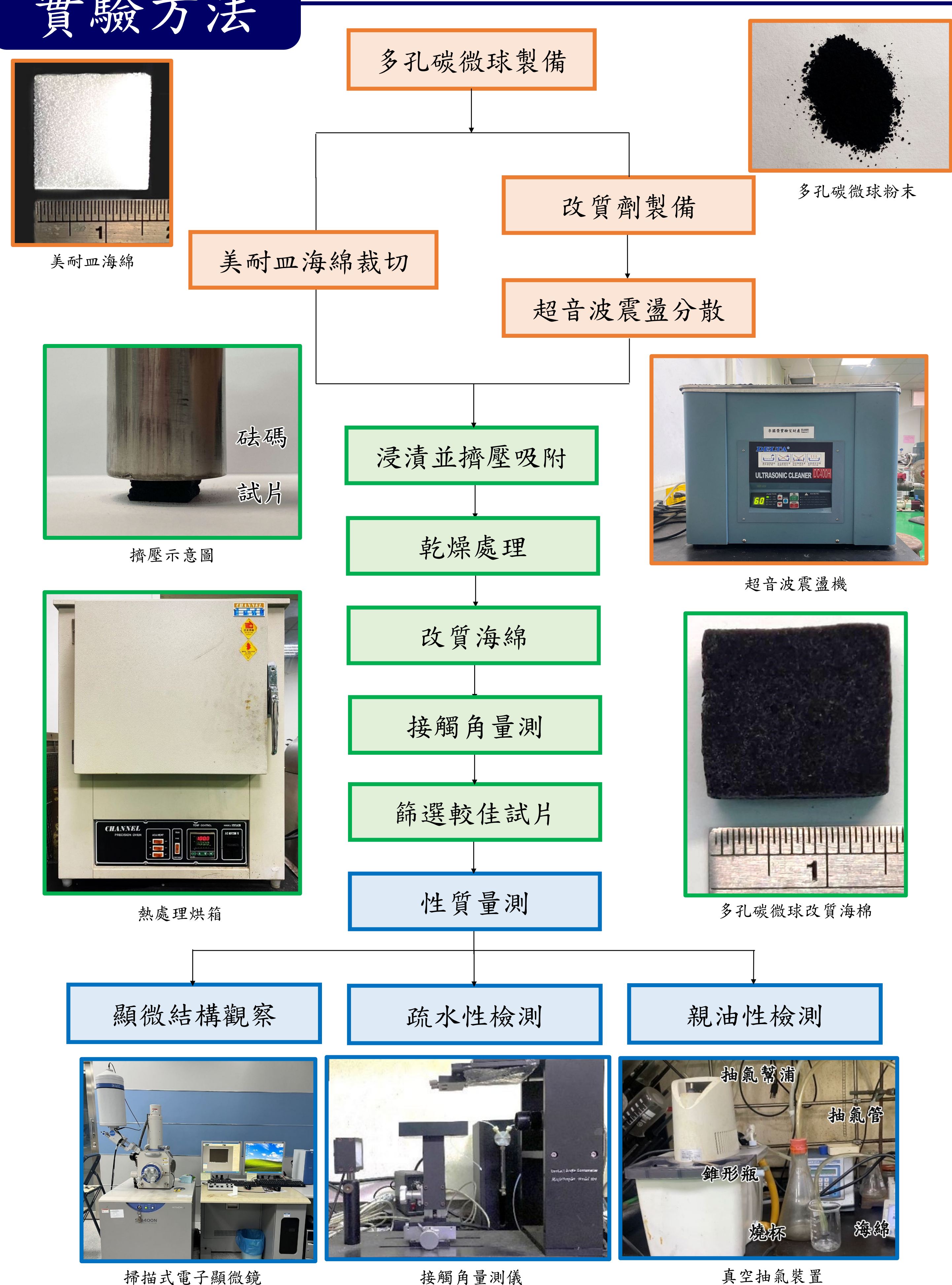


原油污染海洋



超疏水荷葉

實驗方法



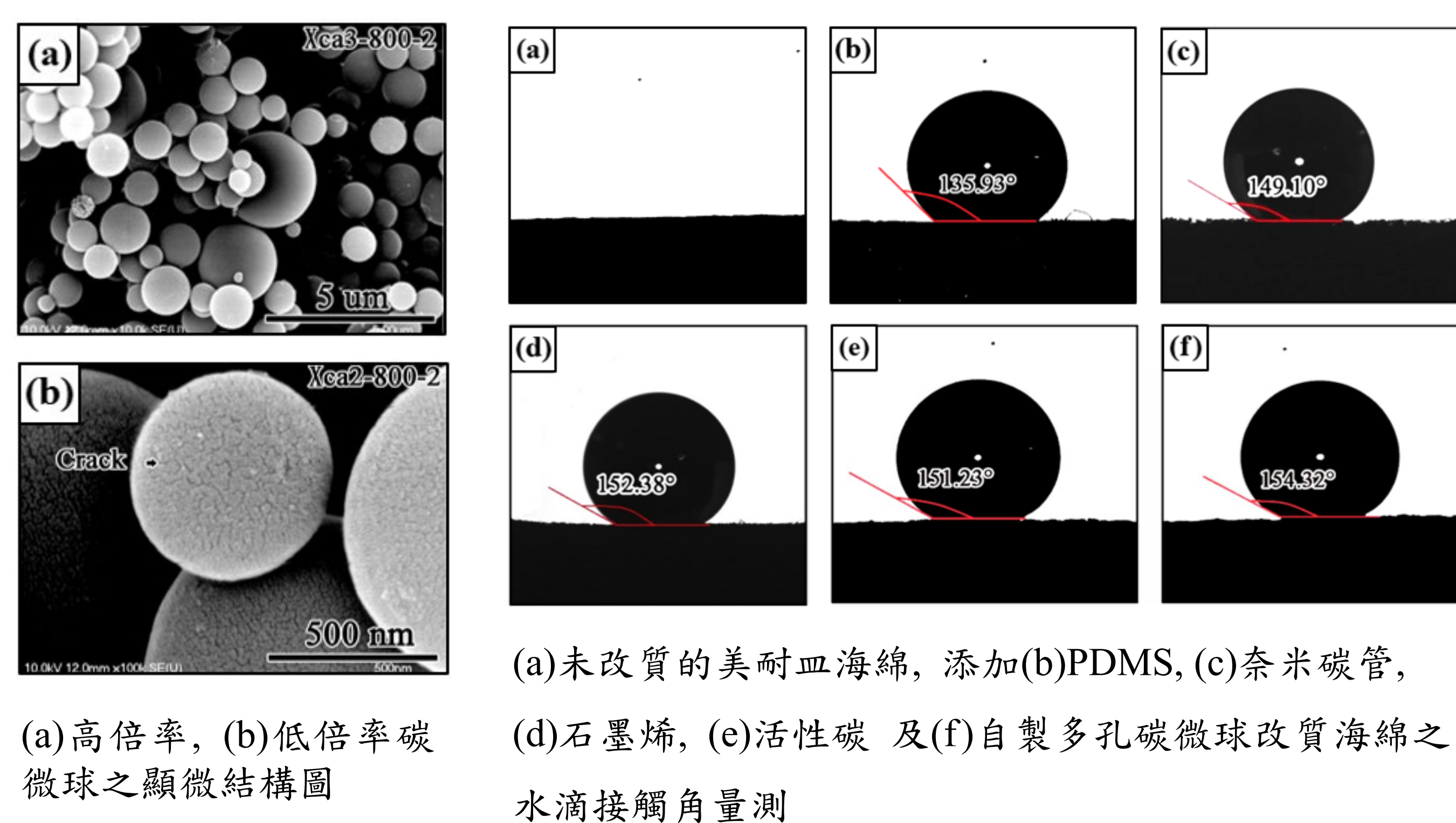
結論

- 以自製多孔碳微球改質之試片，其接觸角大於相同比例之奈米碳管、石墨烯及活性炭，**疏水效果較佳**。
- 適量的碳微球(0.6 g)，可增加材料表面粗糙度，接觸角較大(疏水效果佳)，但碳微球比例若過高，反而造成試片的疏水性降低。
- 自製多孔碳微球改質試片於溫度、曝曬/暴露、海水搖晃及連續壓縮測試下，接觸角(疏水性)皆無明顯變化，**環境適應能力佳**。
- 自製多孔碳微球改質試片透過真空抽氣裝置可**快速連續油水分離**。

誌謝

在此由衷感謝義守大學貴儀中心提供量測設備與儀器及科技部計畫(MOST 110-2221-E-214-003)，使本研究順利進行各項實驗，僅此致謝。

結果與討論



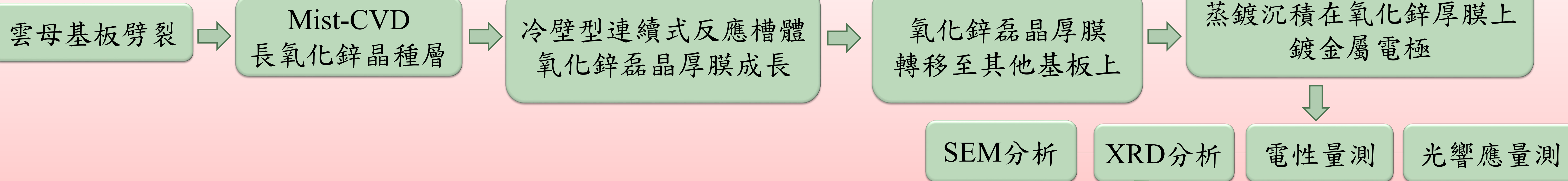
一、前言

指導教授：陳厚光博士

基板 採用柔性雲母基板可將元件用於**可撓式穿戴產品**中。雲母基板與氧化鋅磊晶薄膜間的**凡德瓦作用力**使兩者間晶格匹配度限制降低，因此可將氧化鋅膜層轉移至矽基板上。

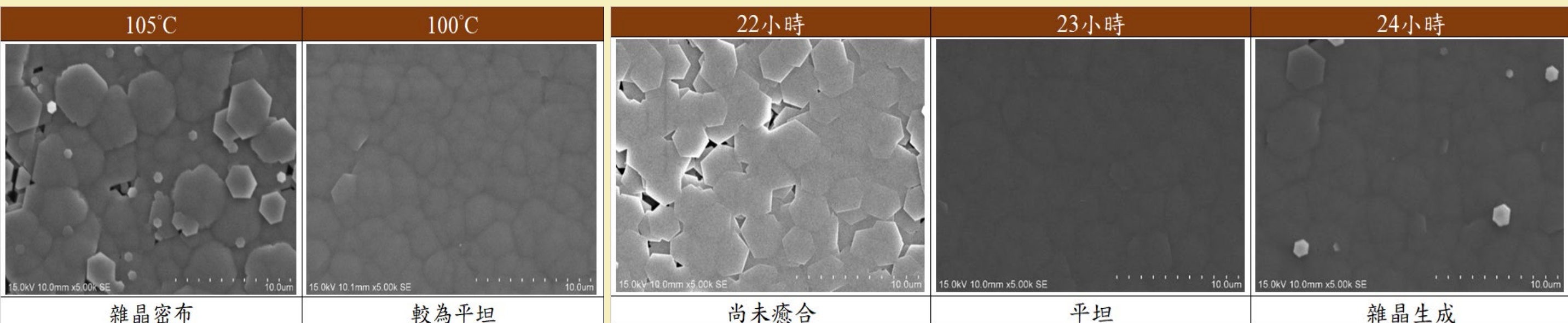
2. 利用射頻濺鍍沉積法成長高溫晶種層，再利用霧化化學氣相沉積法成長氧化鋅磊晶薄膜。

二、實驗步驟



三、結果與討論

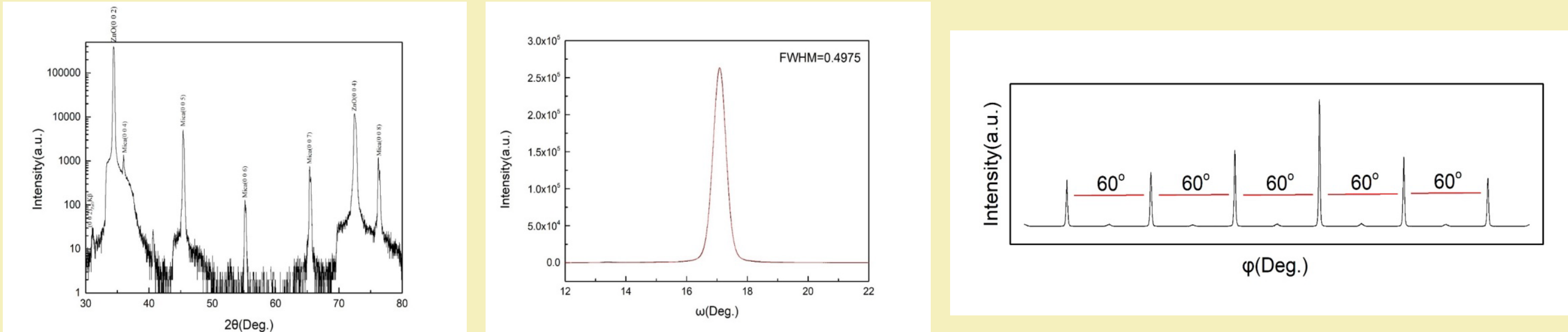
1. 在**100°C**、**23hr**成長條件下可生長出較為優異的氧化鋅磊晶薄膜。



圖二、固定23hr下不同生長溫度之表面SEM觀察

圖三、固定100°C下不同生長時長之表面SEM觀察

1. 透過XRD 2 θ scan分析：可觀察到(0002)ZnO繞射峰強度明顯高於其他峰，證明氧化鋅膜層沿著c軸外延優選(002)方向生長。
2. 透過XRD Rocking curve圖譜分析：可得(10 $\bar{1}$ 1)ZnO繞射峰半高寬(FWHM值)為0.4975°。
3. 透過XRD phi-scan分析：分析ZnO (10 $\bar{1}$ 1)面確定氧化鋅磊晶膜呈規則六重對稱排列，顯示出在雲母基板上成長之氧化鋅磊晶膜層仍維持in-plane規則排列。



氧化鋅膜層 XRD 2θ scan 分析

氧化鋅膜層 Rocking curve 分析

氧化鋅膜層 XRD之ZnO(10 $\bar{1}$ 1)面之phi-scan分析

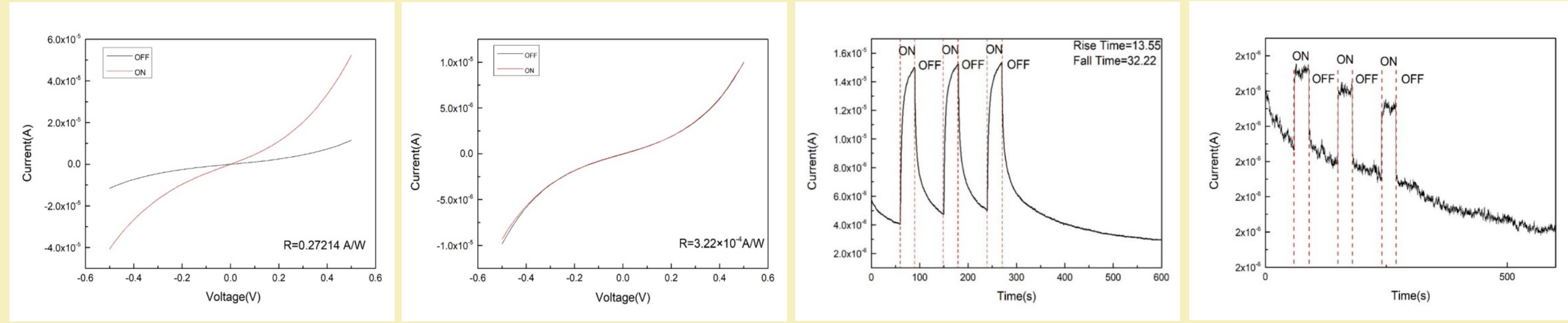
1. 轉移後的膜層其遷移率、電阻值及載子濃度皆因轉移過程影響，證明**轉移膜層後膜層品質會受影響**。

轉移前之霍爾量測				轉移後之霍爾量測			
	Mobility (cm ² /V-s)	Resistivity (Ω-cm)	Bulk concentration (cm ⁻³)		Mobility (cm ² /V-s)	Resistivity (Ω-cm)	Bulk concentration (cm ⁻³)
平均值	37.2	3.76x10 ⁻³	~4.99x10 ¹⁹	平均值	48.0	3.80x10 ⁻³	~5.34x10 ¹⁹
標準差	11.81817146	2.09x10 ⁴	1.98x10 ¹⁹	標準差	27.9527242	2.26x10 ⁴	4.14x10 ¹⁹

表一、轉移前後之霍爾量測

1. 兩者間拒斥比=845.16dB。

2. 可明顯看出氧化鋅膜層對UV光響應明顯，對藍光只有極微小的響應。



膜層照射UV光之I-V曲線圖 膜層照射藍光之I-V曲線圖 膜層照射UV光之I-t曲線圖 膜層照射藍光之I-t曲線圖

六、結論

1. 在 **100°C、23hr** 成長條件下可生長出較為優異的氧化鋅磊晶薄膜。**時長不夠膜層癒合不完全**，因實驗使用的是**化學水浴法**，若溫度過高易導致**化學溶液過早反應**或是**反應劇烈**，而超過適當的磊晶時長則會過度成長，兩者皆會使磊晶成長後的氧化鋅膜層表面不平坦且雜晶密布。

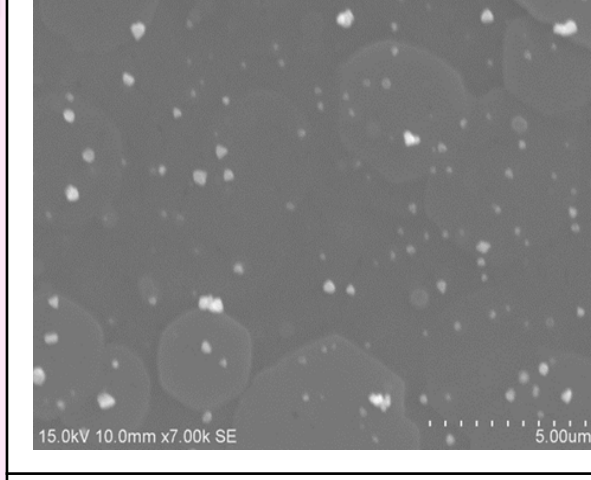
2. 利用氧化鋅與雲母基板間**凡德瓦鍵結**的特點，使用簡易**機械剝離法**將氧化鋅磊晶厚膜轉移至矽基板上，透過霍爾量測可以發現，**轉移後**的氧化鋅磊晶膜層其遷移率、電阻率及載子濃度皆**會受到影響**使其**品質較轉移前差**。

3. 利用光響應量測後做出的I-V、I-t曲線圖可以出對UV光有明顯的響應其R值為0.27214A/W。而對藍光只有些微響應，其R值為0.000322A/W，推測應是本實驗所使用的冷壁式連續流動反應槽所磊晶出的氧化鋅厚膜仍存在缺陷，而形成了深層能階使照光時出現響應的情況。

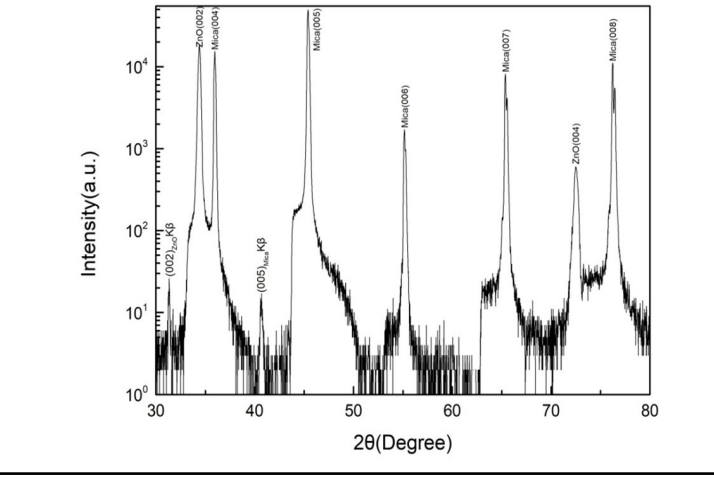
4. 兩種不同彎曲型態(上彎曲及反覆彎曲)的電流-電壓(I-V)曲線皆呈現S形曲線為蕭特基(Schottky)接觸。

實驗二

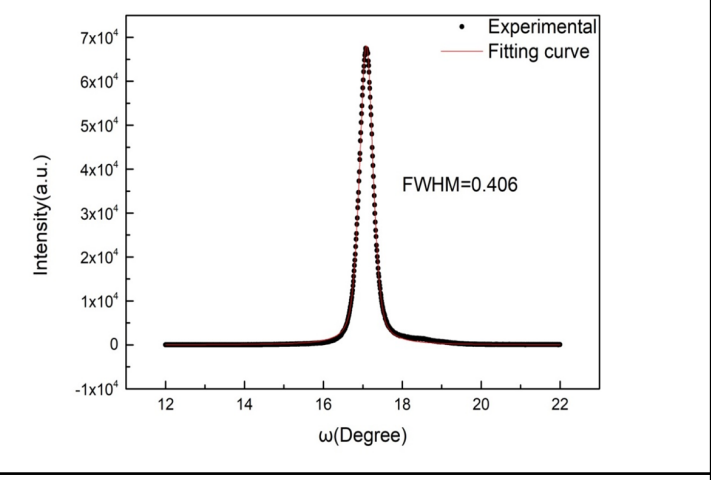
SEM分析



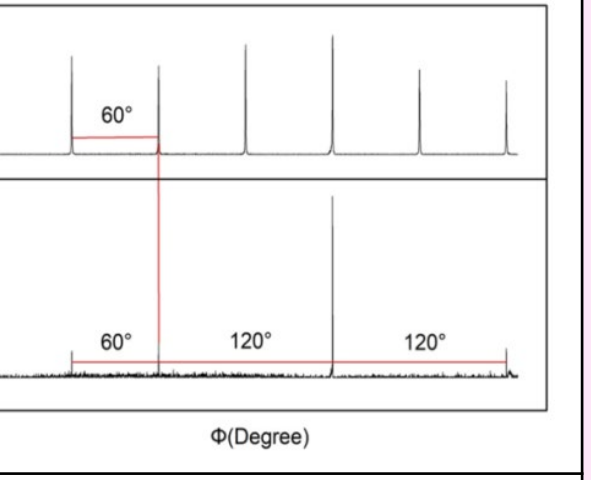
氧化鋅磊晶薄膜平坦
且均勻、癒合度佳。



ica(005) 面之繞射峰的強度大於 ZnO(002) 面之繞射峰訊



氧化鋅ZnO(002) 面的繞射峰之半高寬值為0.406°。



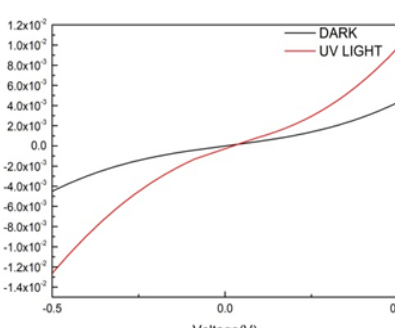
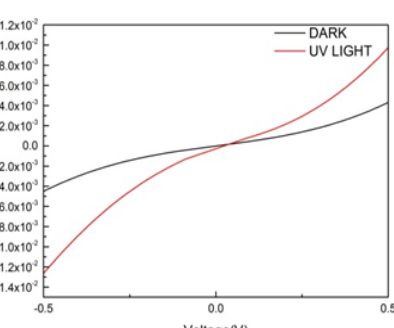
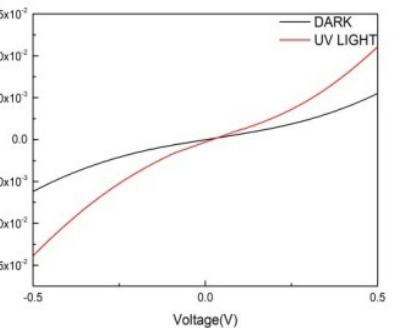
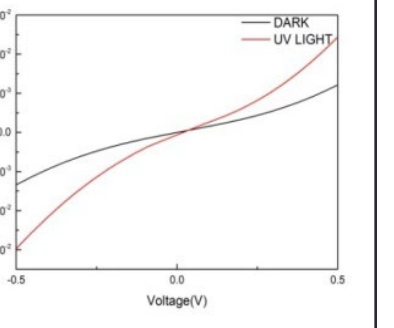
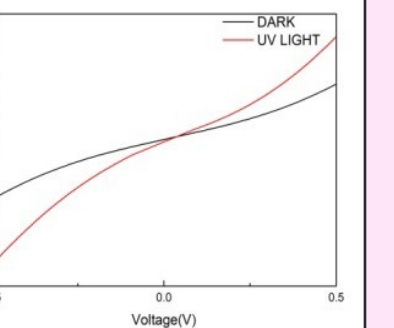
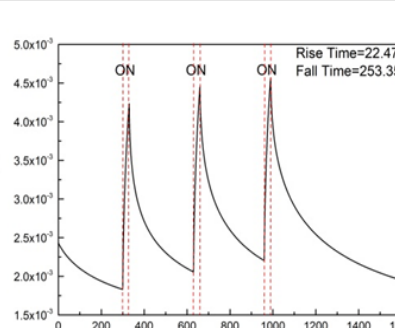
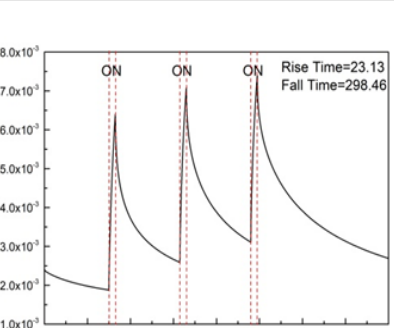
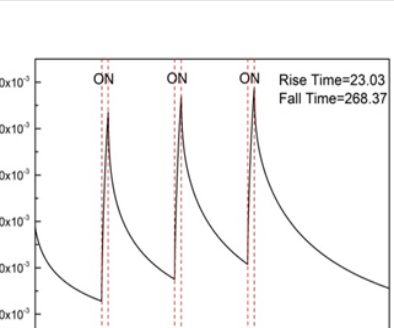
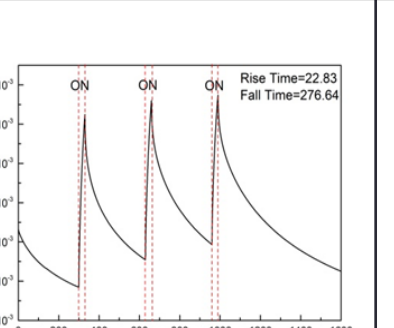
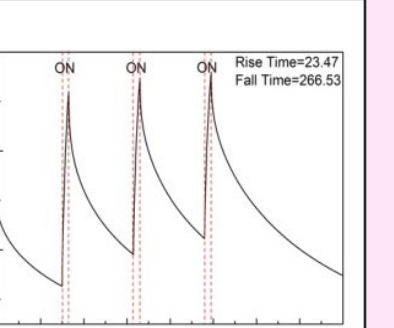
化鋅膜層呈現**六軸對稱**結構。

- **UV-Visible** 穿透光譜分析

1. 薄膜**穿透率**高達為**59.222%**。
2. 薄膜**UV-可見光光能隙**值為**3.28eV**。

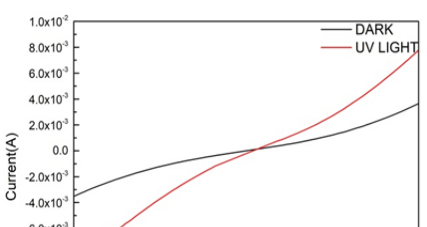
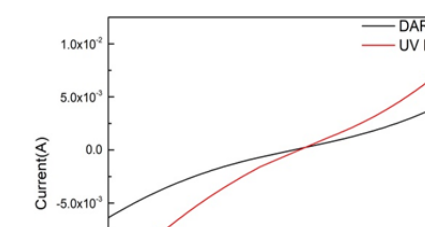
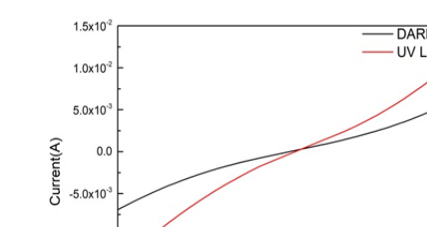
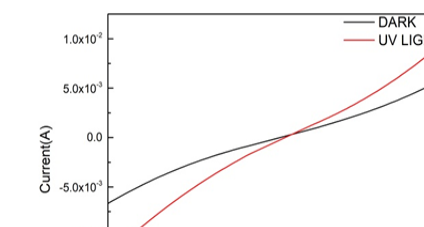
- 上彎曲電流-電壓(I-V)曲線及電流-時間(I-T)曲線量測分析

1. 上彎曲在不同曲率的比較測試時，其R值與D*值皆差異不大。
2. 上彎曲在不同曲率的比較測試時，**PDCR 有些微隨著曲率半徑變小而有變小的趨勢。**
3. 上彎曲電流-時間(I-T)曲線差異不明顯。

量測順序	一	二	三	四	五
曲率半徑	0(cm)	1.25(cm)	1(cm)	0.75(cm)	0.5(cm)
R(A/W)	36.06	36.06	37.19	39.92	36.69
PDCR	1.26	1.25	1.01	0.97	0.82
D*(Jones)	3.76×10^{11}	3.76×10^{11}	3.43×10^{11}	3.48×10^{11}	3.07×10^{11}
I-V圖					
I-T圖					

- 反覆彎曲(無彎曲-上彎曲-無彎曲-上彎曲)電流-電壓(I-V)曲線及電流-時間(I-T)曲線量測分析

1. 反覆彎曲在不同曲率的比較測試時，其R值與D*皆差異不大。
2. 反覆彎曲在不同曲率的比較測試時，其PDCR會隨著彎曲有些微降低的趨勢。
3. 反覆彎曲的電流-時間(I-T)曲線差異不明顯。

量測順序	一	二	三	四
曲率半徑	0(cm)	1(cm)	0(cm)	1(cm)
R(A/W)	27.19	29.49	33.52	26.86
PDCR	1.11	0.73	0.76	0.62
D*(Jones)	3.07×10^{11}	2.59×10^{11}	2.82×10^{11}	2.28×10^{11}
I-V圖				
I-T圖				



利用常壓Mist-CVD 製程在尖晶石基板上進行 ZnGa_2O_4 磊晶薄膜成長及其深紫外光偵測器應用之研究

Hou-Guang Chen*, Hsu-Cheng Ku, Kai-Chen Yen, Chao-Feng Tsai

摘要

本實驗將採用簡易、常壓、環境友善Mist-CVD製程，在尖晶石基板上進行尖晶石礦氧化鋅鎵(ZnGa_2O_4)的磊晶薄膜成長。並且搭配各種薄膜分析技術 (SEM、XRD、UV-Vis及霍爾效應分析儀)，探討Mist-CVD製程氣氛對於 ZnGa_2O_4 的顯微組織、晶體結構及光電性質影響。此外，進一步進行 ZnGa_2O_4 深紫外光偵測器製作及其深紫外光響應性質研究。

經實驗結果可得知在氮氣氣氛下的氧化鋅鎵(ZnGa_2O_4)表面形貌較不完整，有許多雜晶。在光響應分析與電性量測下發現，兩種氣氛的試片對於UVC光都具有較靈敏的反映，而與氮氣相比;氧氣下的試片具有8.08A/W的光響應度， 4.1×10^5 的光暗電流比，相比於氮氣高出許多。

實驗說明

1. 尖晶石基板製備

- 未退火的a面藍寶石基板利用RF-Sputtering在常溫下沉積 ZnO 薄膜20分鐘。
- 使用高溫爐進行1000°C退火3分鐘。

3. ZnGa_2O_4 薄膜量測

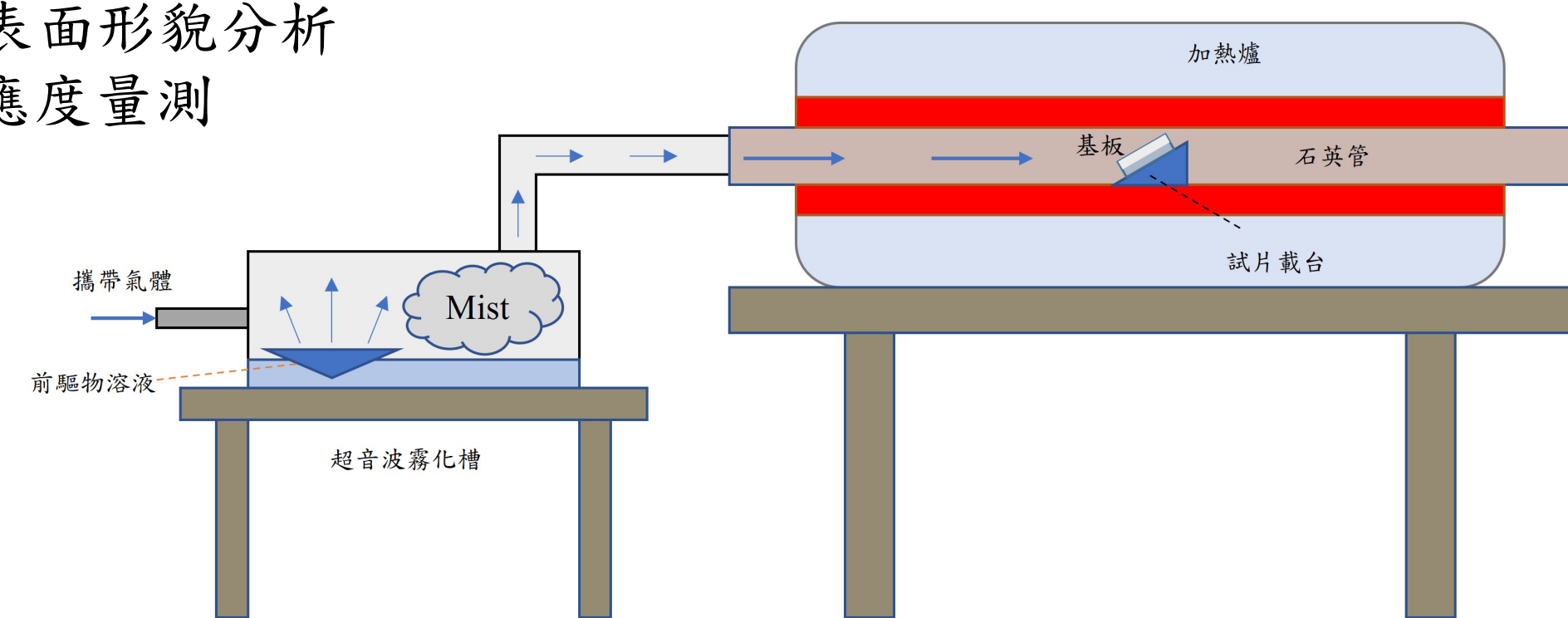
- X-ray 繞射分析
- SEM表面形貌分析
- 光響應度量測

2. ZnGa_2O_4 磊晶薄膜成長

- 前驅物: $\text{Zn}(\text{acac})_2$, $\text{Ga}(\text{acac})_3$ 做為溶質，D.I.水和 2 vol.% HCl 作為溶劑。
- 在600 °C進行60分鐘的 Mist-CVD 成長。
- 攜帶氣體: 氧氣、氮氣。

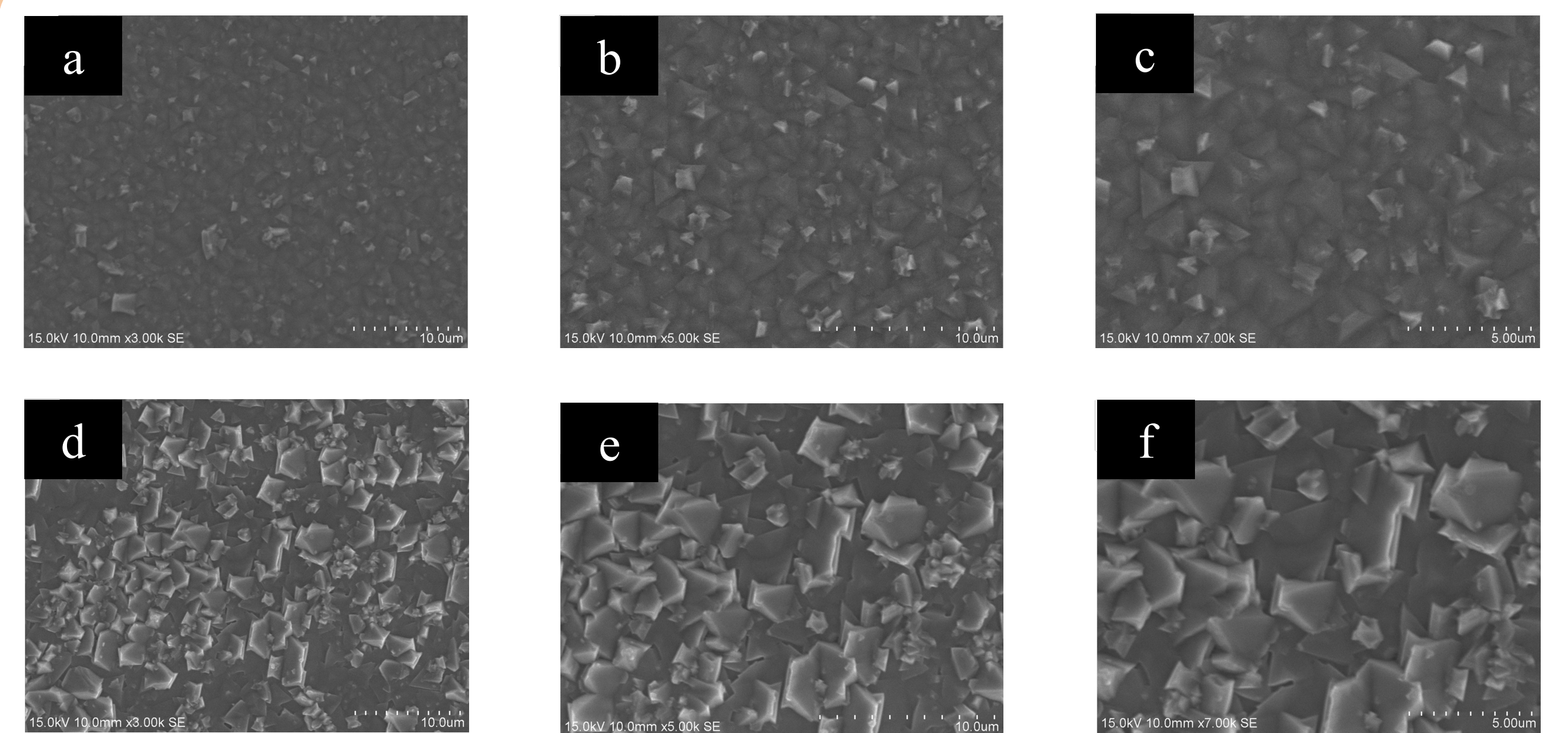
4. MSM 深紫外光偵測器元件製作

- 透過遮罩製作指叉狀的金電極



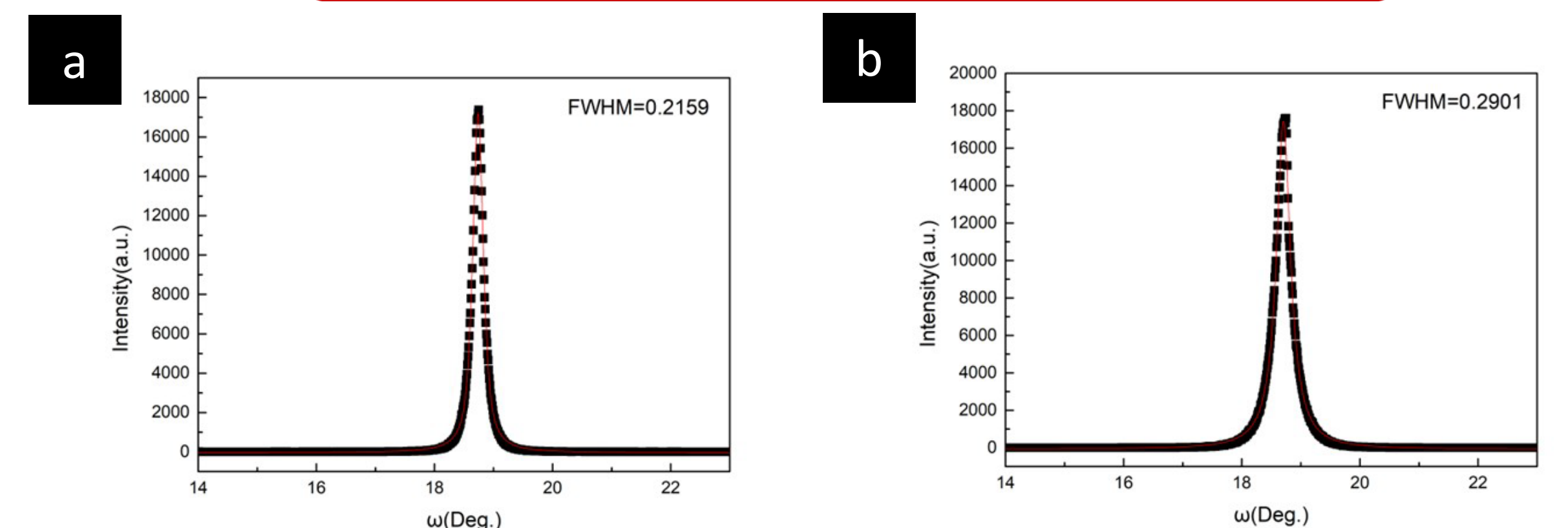
圖一、Mist-CVD 示意圖

SEM表面形貌觀察

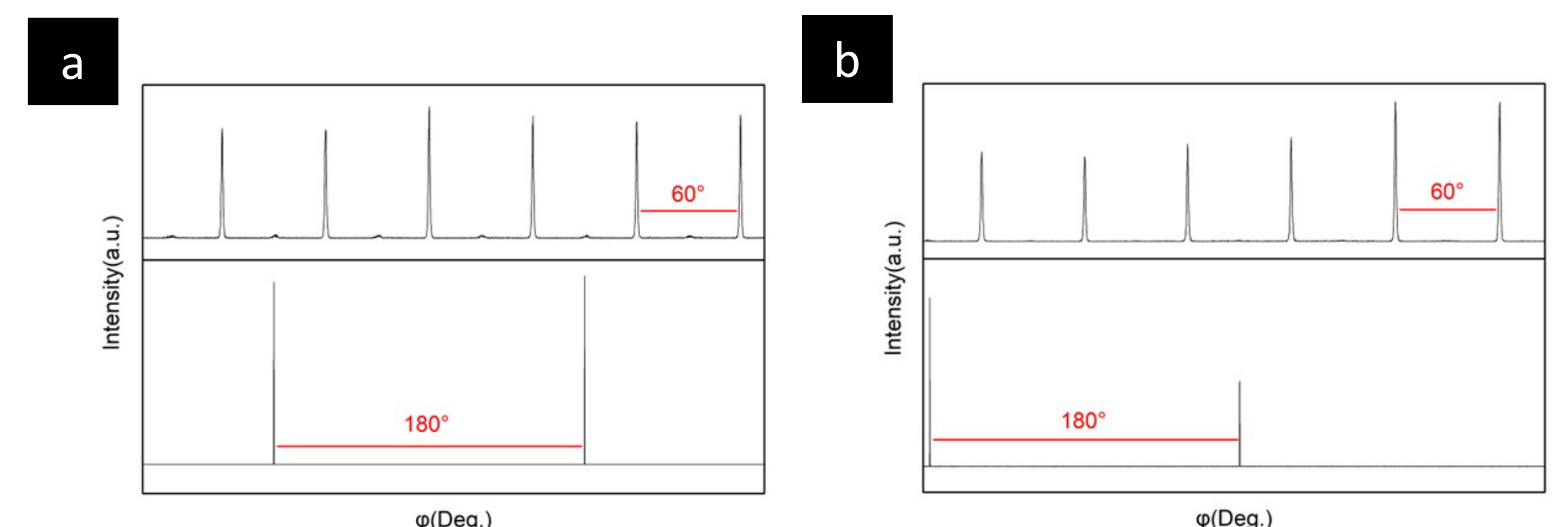


圖二、(a-c)以氧氣為載體進行 ZnGa_2O_4 磊晶成長的表面形貌 (d-f)則是以氮氣為載體進行 ZnGa_2O_4 磊晶成長的表面形貌

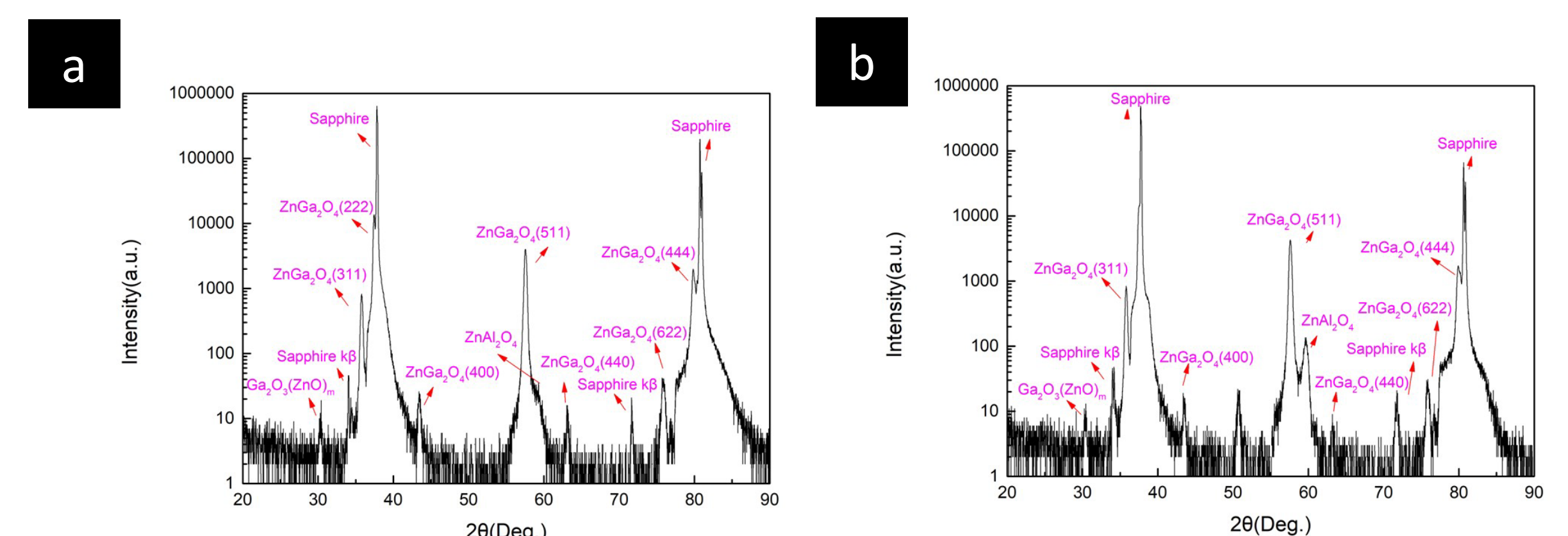
X-Ray繞射分析



圖四、(a)氧氣(b)氮氣氣氛下 ZnGa_2O_4 薄膜的XRD半高寬量測

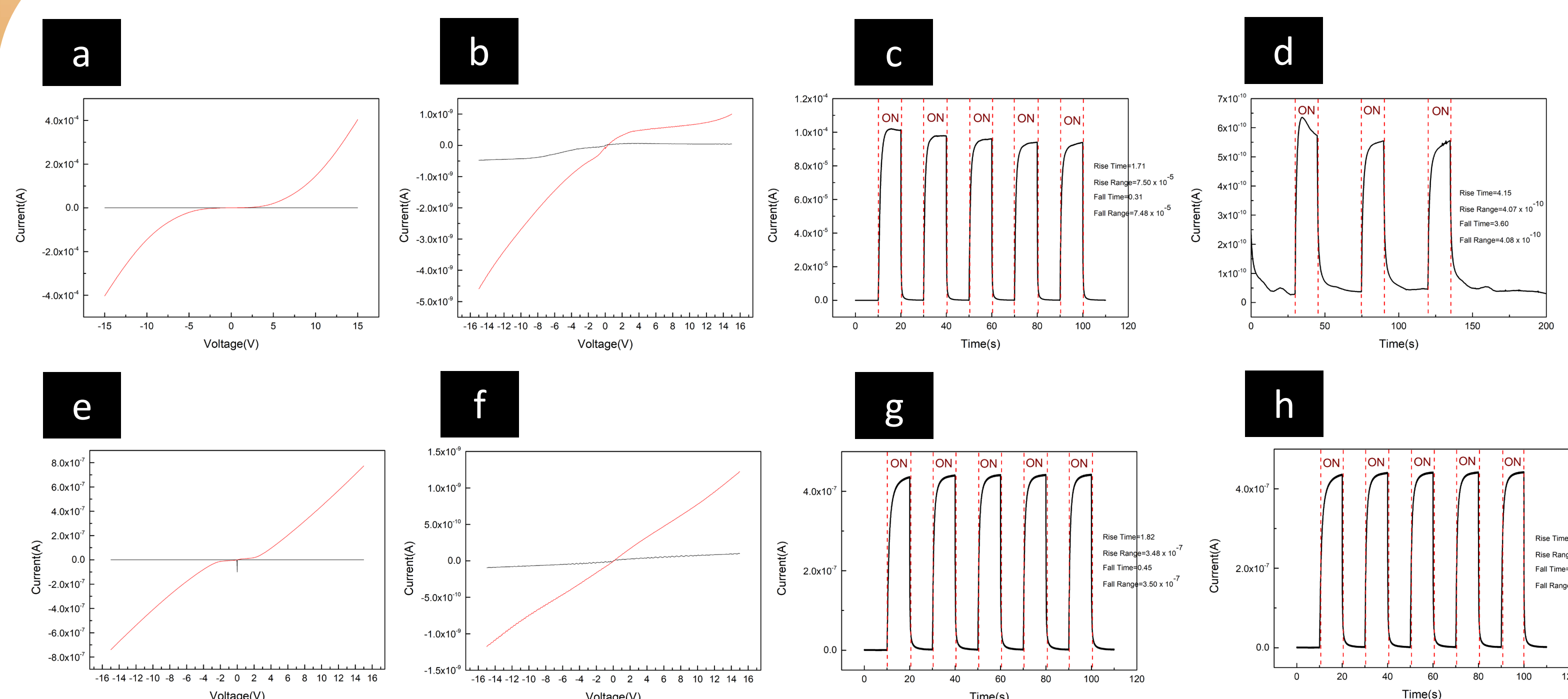


圖五、(a)氧氣(b)氮氣氣氛下 ZnGa_2O_4 薄膜的XRD Phi 掃描



圖六、(a)氧氣(b)氮氣氣氛下 ZnGa_2O_4 薄膜的XRD θ-2θ掃描

光響應特徵



圖三、(a,b)氧氣氣氛下的 UVC及藍光的 I-V圖，(c,d)氧氣氣氛下的 UVC及藍光的 I-T圖 (e,f)氮氣氣氛下的 UVC及藍光的 I-V圖，(g,h)氮氣氣氛下的 UVC及藍光的 I-T圖

表一、光響應度特徵結果

	UVC (O_2)	Blue (O_2)	UVC (N_2)	Blue (N_2)
Wavelength(nm)	260	467	260	467
$I_{\text{dark}}(\text{A})$	9.78×10^{-10}	4.76×10^{-10}	1.38×10^{-10}	1.02×10^{-10}
$I_{\text{light}}(\text{A})$	4×10^{-4}	4.58×10^{-9}	7.69×10^{-7}	1.22×10^{-9}
$I_{\text{photocurrent}}(\text{A})$	4×10^{-4}	4.1×10^{-9}	7.69×10^{-7}	1.12×10^{-10}
Photo power(mW/cm ²)	0.33	0.905	0.33	0.905
R(A/W)	8.08	3.02×10^{-5}	1.56×10^{-2}	8.24×10^{-6}

結論

透過SEM分析結果，在氧氣氣氛下的表面形貌較為平滑，氮氣下的表面則較多雜晶。試片進行XRD半高寬分析氧氣下的試片為0.2159°，氮氣下則為0.2901°進行Metal-Semiconductor-Metal(MSM)光偵測器元件製作與分析，得知試片相對UVC光有較明顯的反應。從I-T圖發現氧氣的上升速率為1.71秒;下降速率為0.31秒。經電性量測後得知氧氣下UVC光的照射發現有8.08A/W的光響應度。氧氣相對於氮氣有較卓越的表現。

以磁性智慧複合奈米粒子萃取癒傷組織分化葉中 人參皂苷Rg 1及其治療心肌細胞的缺氧損傷

Chian-Jin Tzeng¹, Ching-Yi Chang¹, Yu-Tzu Chu¹, Min-Ru Hsu¹, Shou-Sheng Fang¹ and Mei-Hwa Lee^{1*}

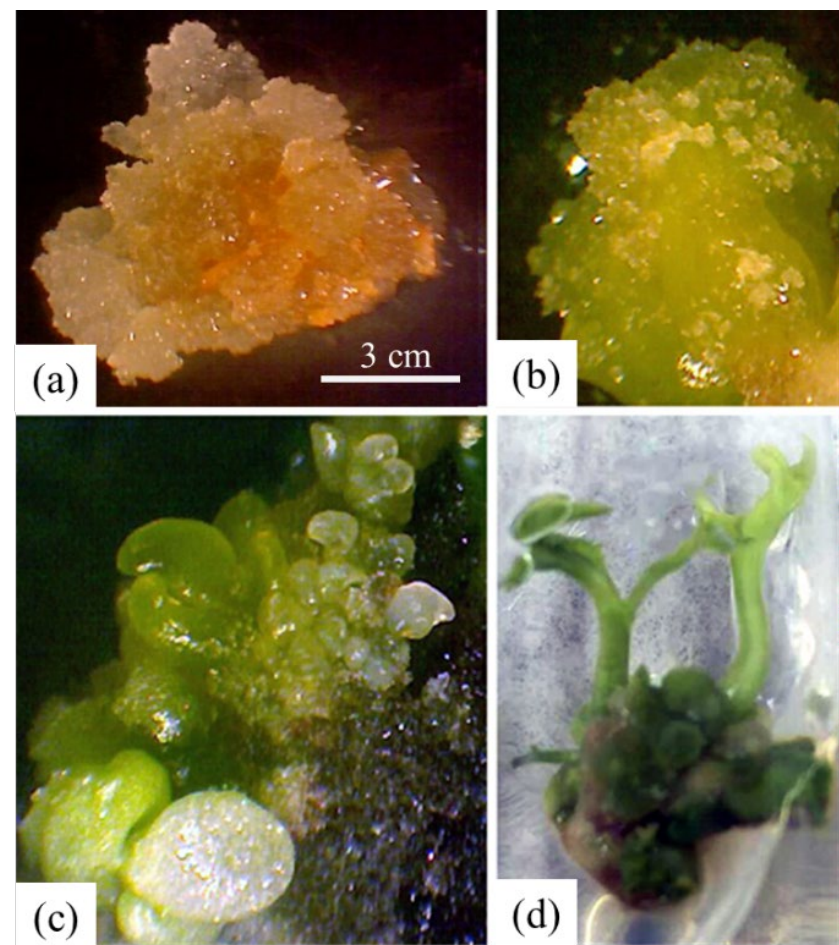
¹Department of Materials Science and Engineering, I-Shou University, Kaohsiung 84001, Taiwan

人參在傳統醫學中為補營養物質，擁有補氣的功效，受損器官功能的修復，以及提高細胞的活力，然而人參中最有效的是癒傷組織中的人參皂苷。根據現代藥理研究報導，**人參皂苷**(例如:Rg、Re)可以強化心臟之收縮舒張力，改善心衰竭之狀態。本實驗使用的植物材料為三年生之人參根，主要將其進行表面消毒後於培養基中進行培養，希冀獲得許多人參癒傷組分化根針對心肌細胞進行有效的修復。

藉由分子拓印技術將**Rg1 MIPs**分別拓印於27%聚乙烯醇奈米粒子之上，並且可得知利用粒徑分析之方法測量拓印Rg1 MIPs磁性奈米粒子之洗前、洗後及再吸附粒徑分別為**85.8±6.07**、**142.25±6.15**及**105.1±4.94 nm**，然而拓印粒子在移除拓印分子時會有團聚現象，而再吸附胜肽使粒子具有較佳的分散性，導致**再吸附後的粒徑會較洗後粒徑低**。本實驗利用吸附於Rg1 MIPs，以及未拓印模板(NIP)上，吸附30分鐘後，加藥於24 well細胞盤中，經過五天的觀察，進行Jc-1染色以及細胞生長測定CCK-8。並利用HPLC儀器檢測出人參葉浸泡液成分為**Rg1**，吸附**Rg1奈米粒子在第五天有顯著修復損傷心肌細胞**。

實驗步驟

人參癒傷組織再分化成葉

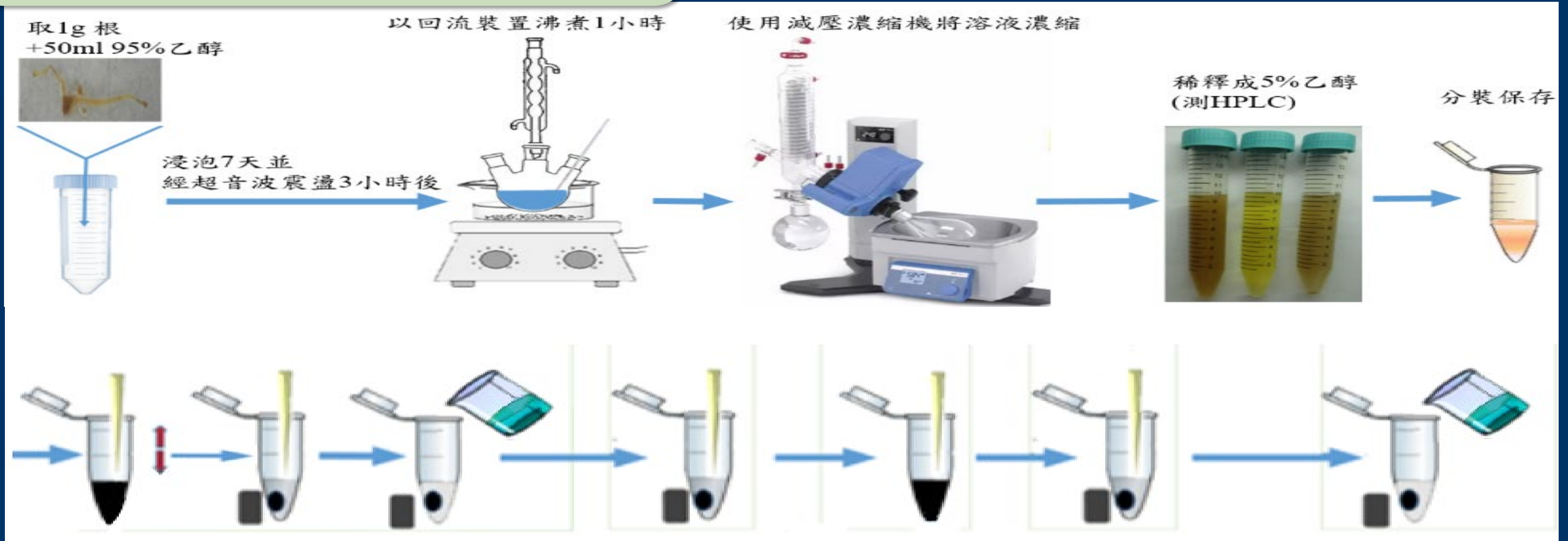


癒傷組織

naphthaleneacetic acid (4mg/L)
培養2個月

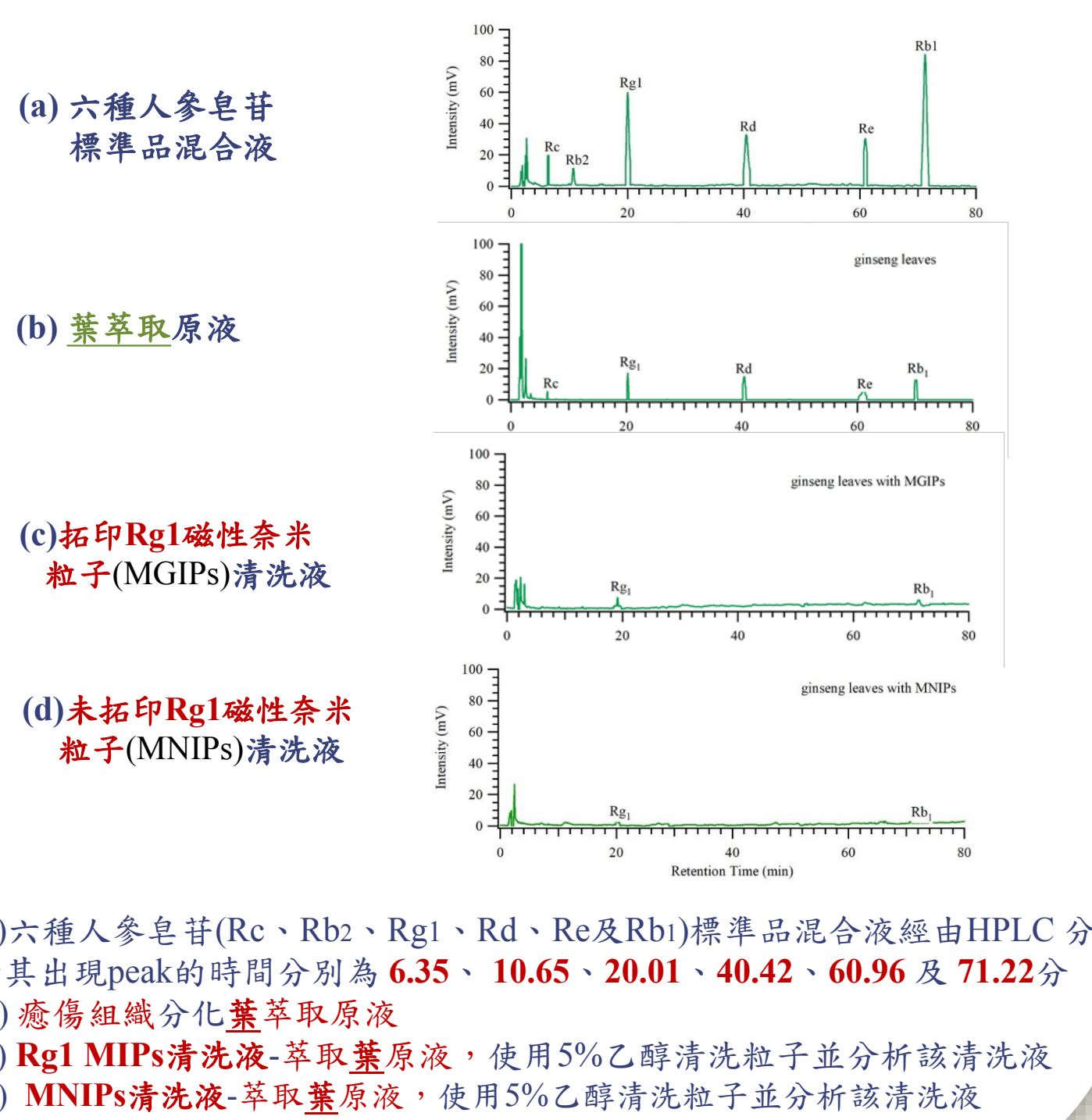
葉

萃取人參皂苷的實驗流程圖



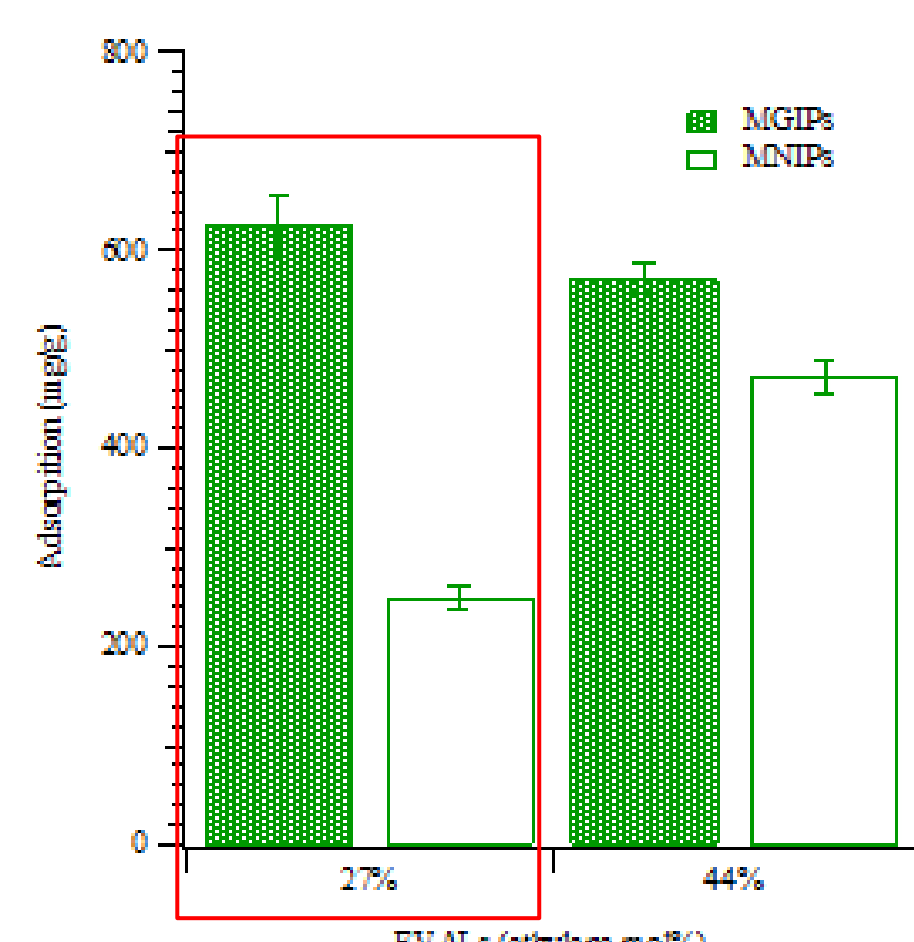
實驗結果

拓印Rg1磁性奈米粒子吸附人參葉 萃取原液(HPLC 分析吸附人參皂苷)



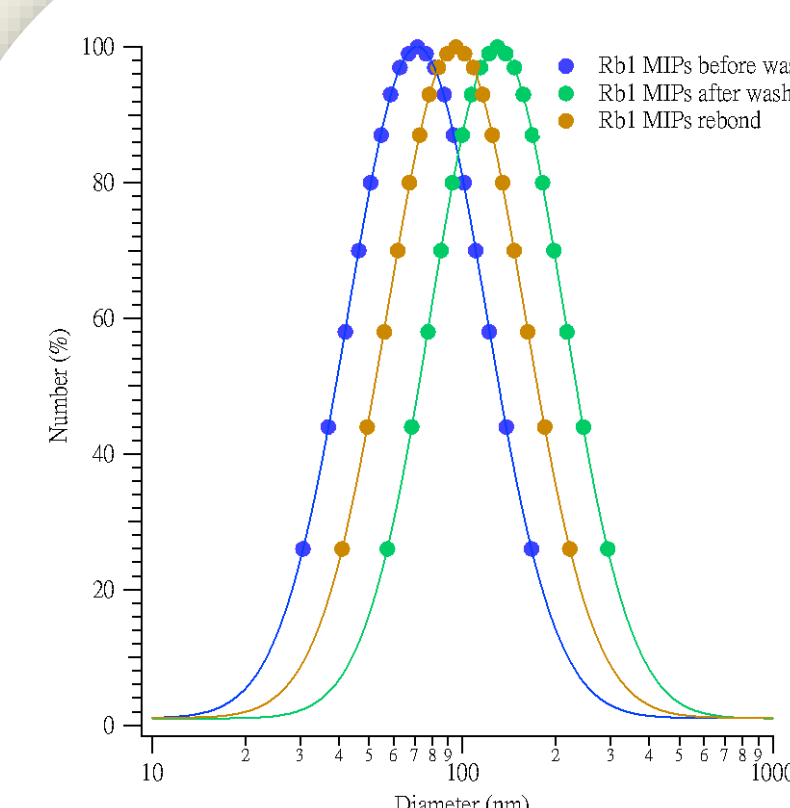
聚乙烯醇醇中乙烯基耳比改變之影響

拓印效率 α =MGIPs之吸附量/MNIPs之吸附量

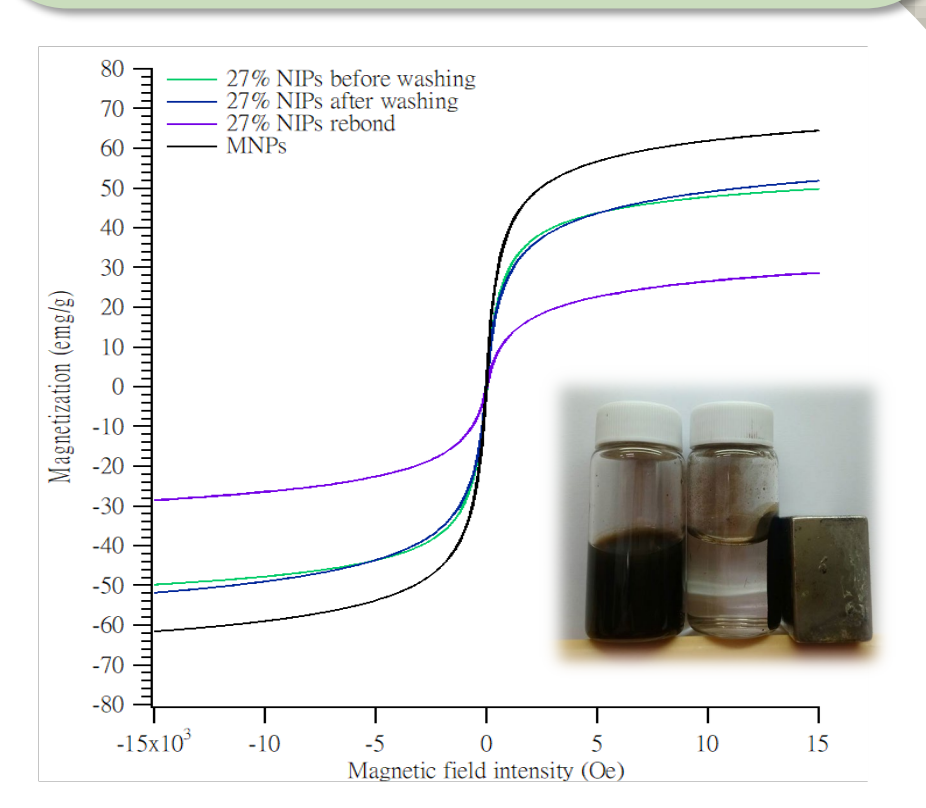


由數據分析可表示，拓印效率 α 值由聚乙烯醇醇中乙烯基之比例依序遞增的拓印效率 α 值為2.5及1.2，其中較佳者為拓印27%聚乙烯醇奈米粒子之拓印效率 α 值2.5，因此選用拓印27%聚乙烯醇奈米粒進行後續吸附曲線等試驗。

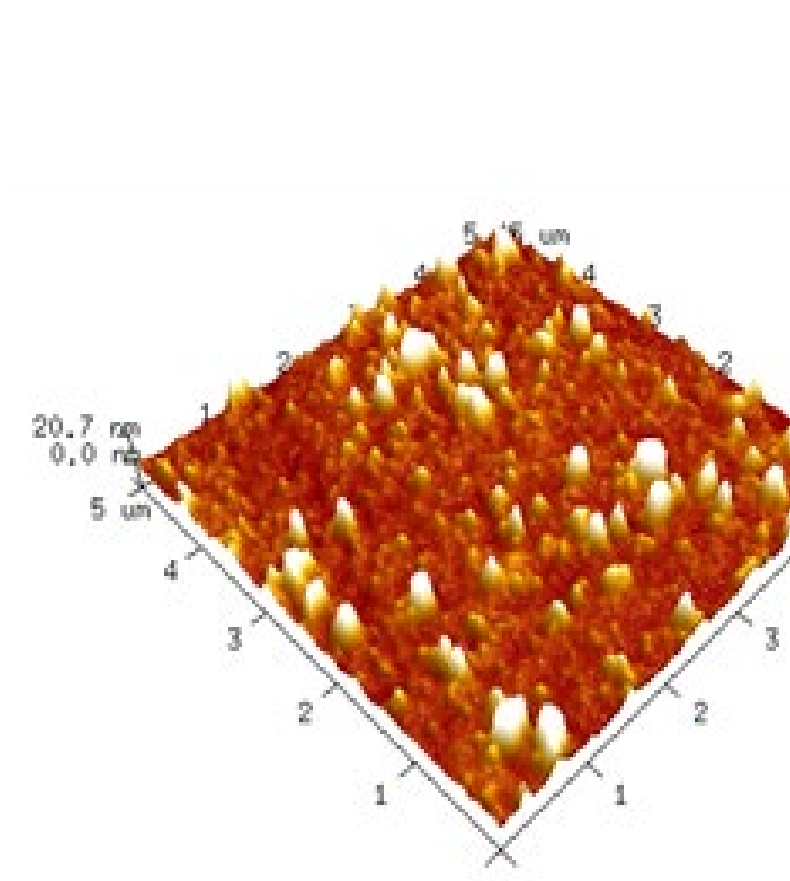
粒徑分析



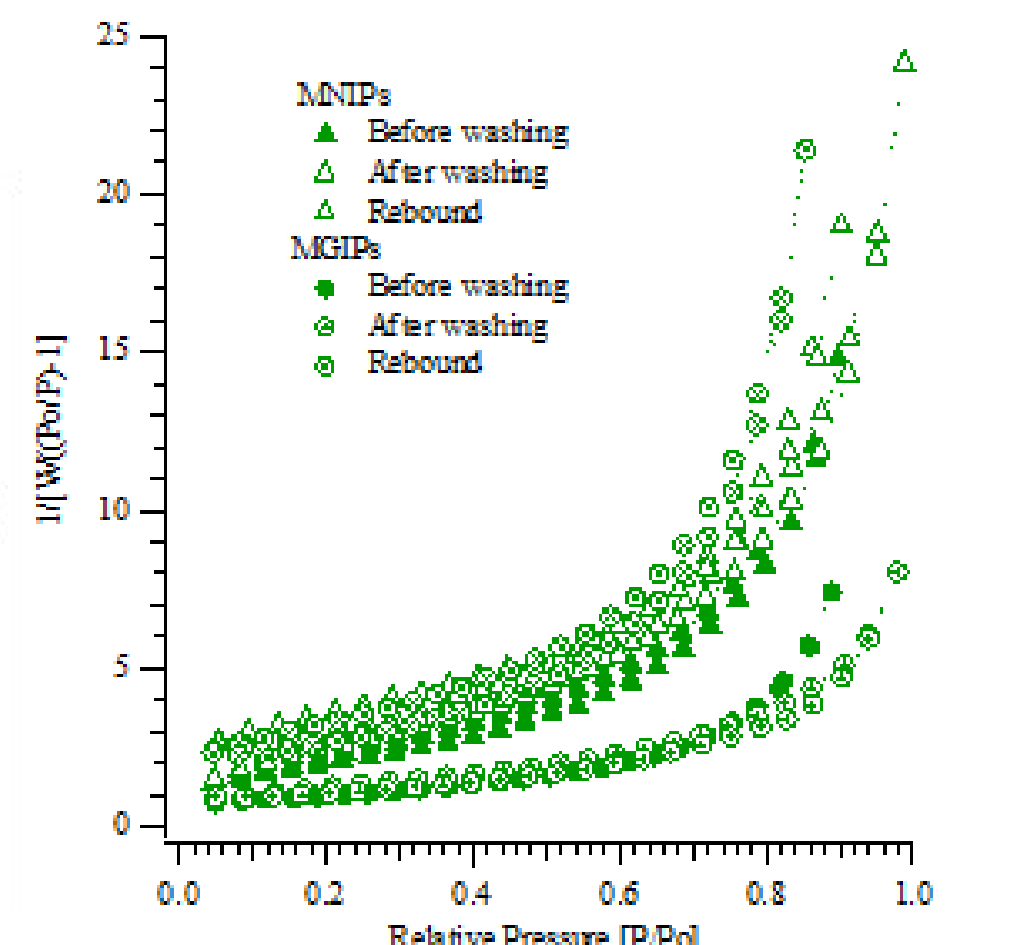
磁性測量(SQUID)



AFM

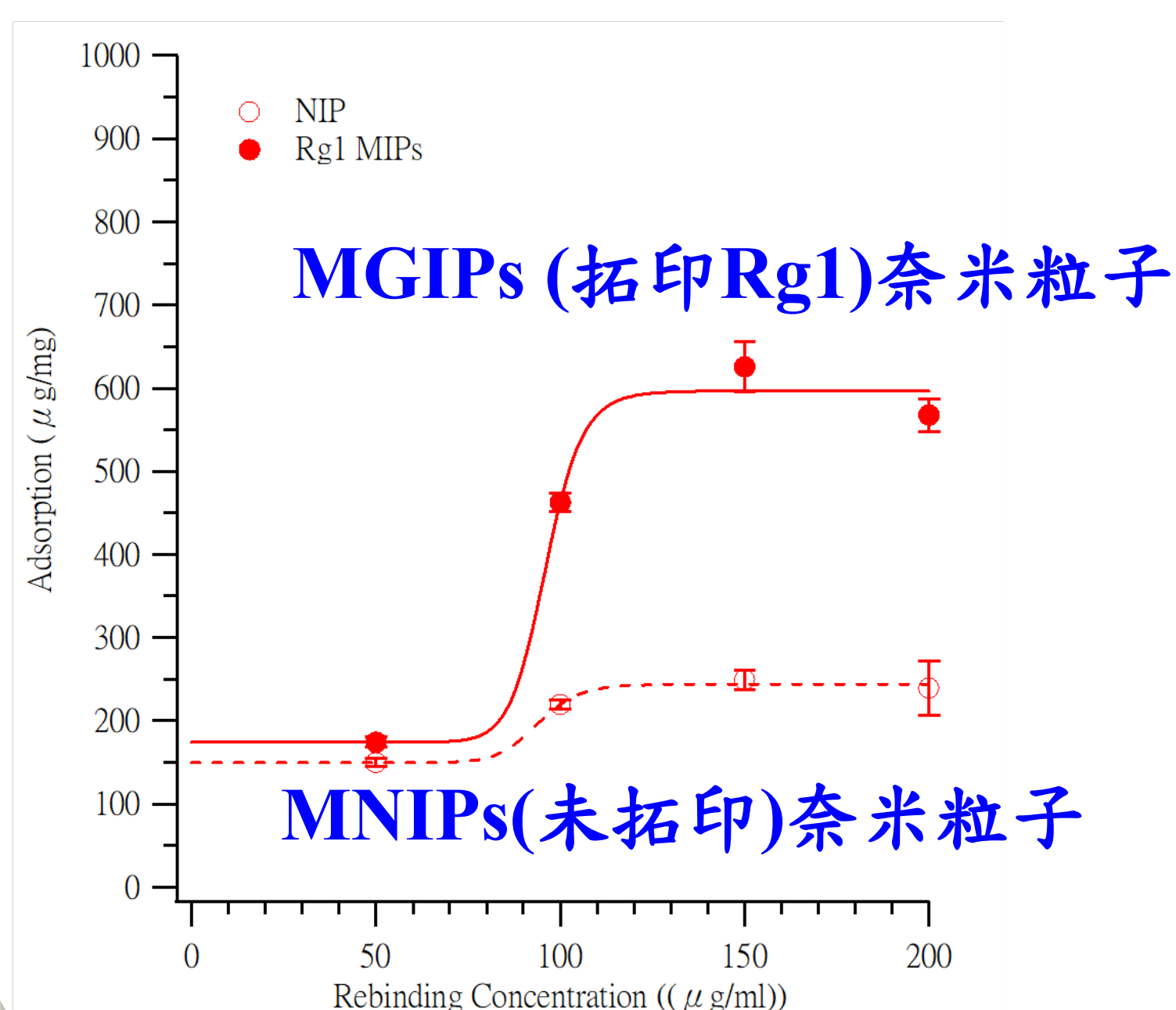


比表面積分析(BET)

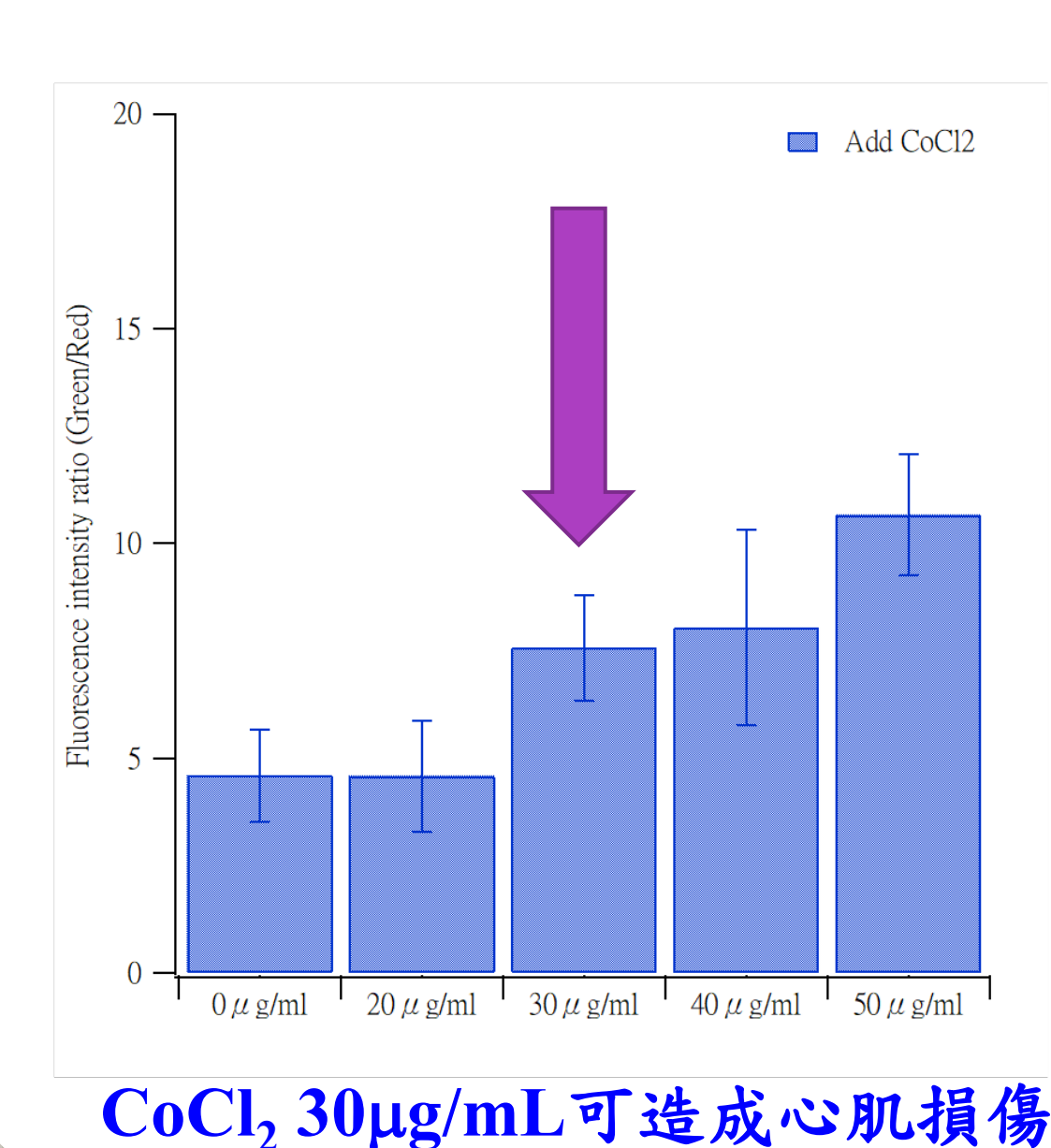


拓印Rg1之27%聚乙烯醇MGIPs

吸附曲線

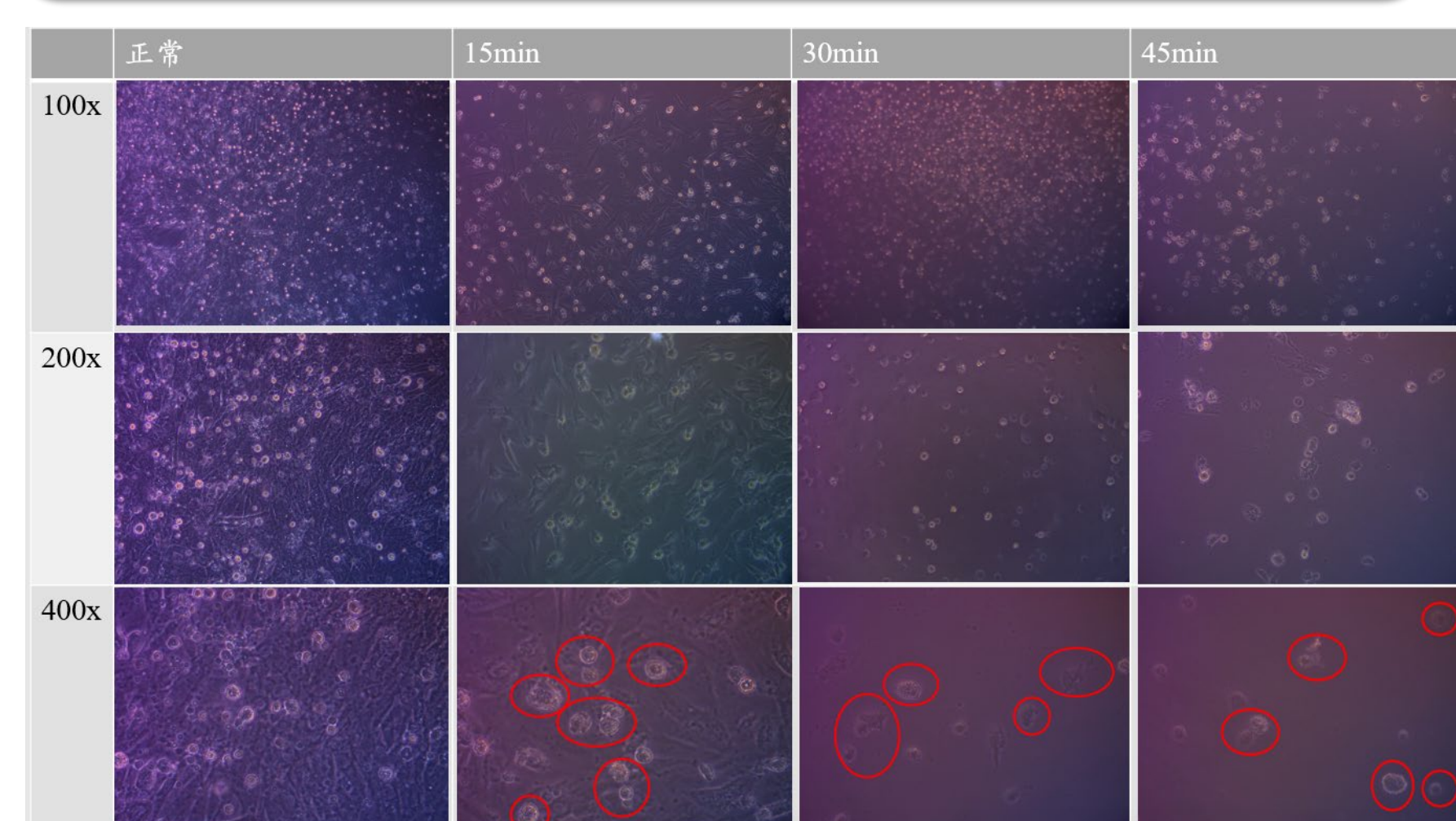


CoCl₂造成心肌細胞H9c2損傷濃度



CoCl₂ 30 μ g/mL可造成心肌損傷

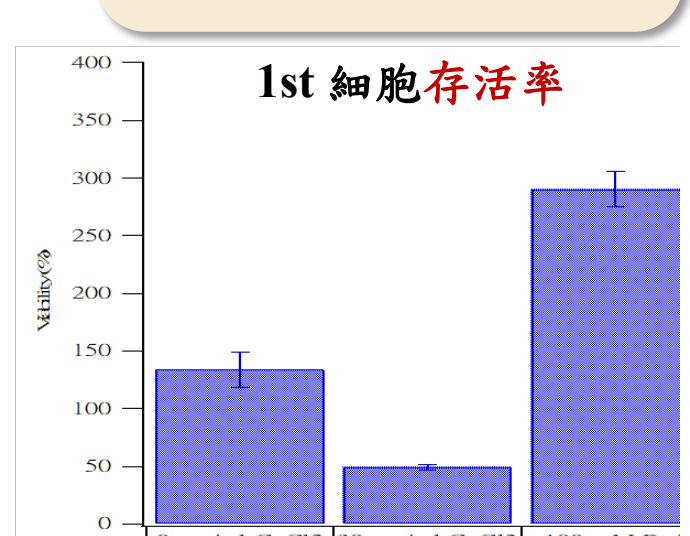
CoCl₂造成心肌細胞H9c2損傷時間



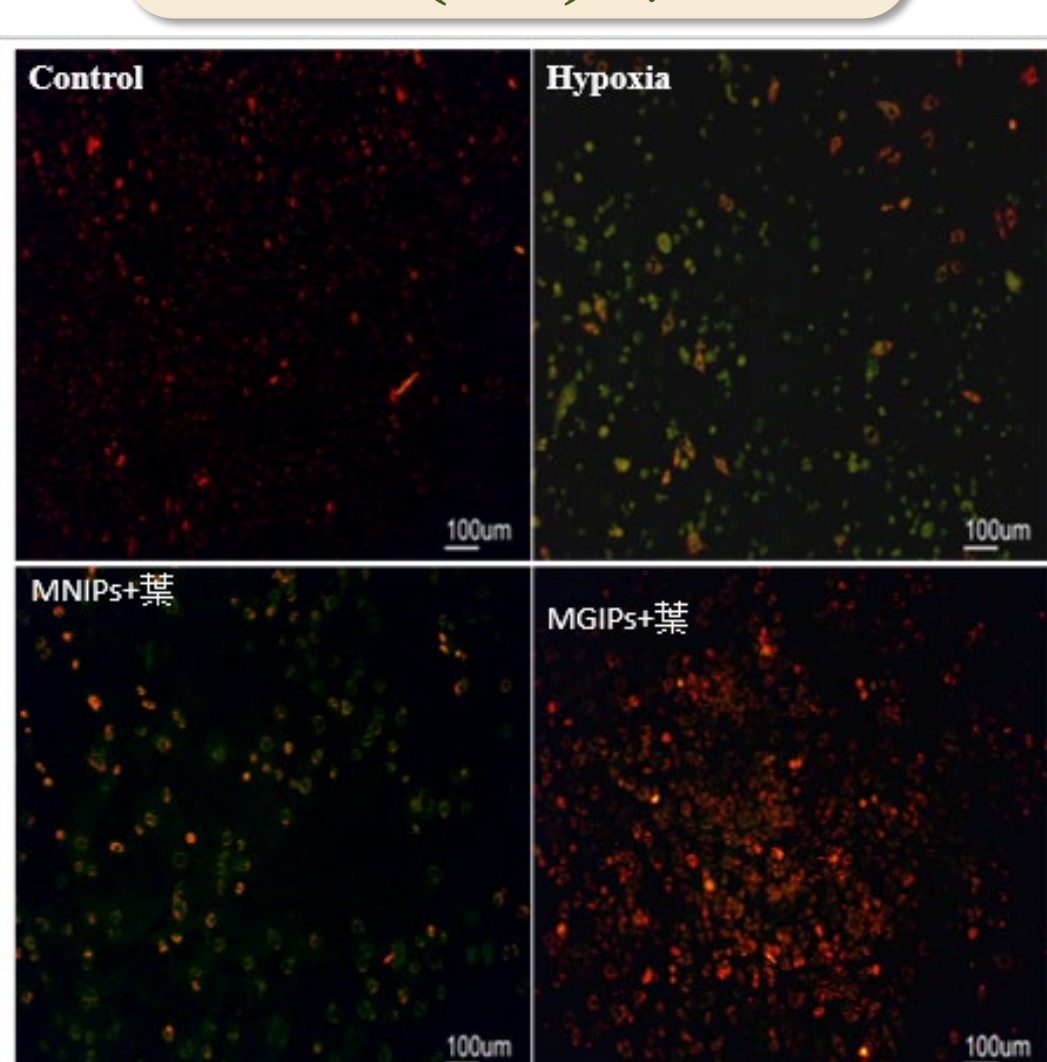
圈起來為細胞損傷，
但時間越久損傷細胞會死亡
之後實驗以30分鐘

以MGIPs萃取分畫葉對H9c2損傷修復

cc-kit 8



Jc-1(5th)染色



有吸附葉萃取液
的MGIPs
在第五天已經恢復
心肌細胞功能

觀察加入的藥物對受損細胞修復
(綠色受損細胞，紅色健康細胞)

結論

利用分子拓印技術將MGIPs分別拓印於27%聚乙烯醇奈米粒子之上接著使用粒徑分析、高效能液相分析、CCK-8、比表面積以及磁性測量等各項分析，發現人參中的癒傷組織成分MGIPs對於修復心肌細胞是有顯著的功効的，並且從Jc-1染色**第五天**可看出MGIPs修復細胞的效果較為顯著，由實驗得出已拓印Rg1的磁性奈米粒子且進行再吸附比其他未拓印或未吸附更具有超順磁性，磁通量為63.69 emu/g，使MGIPs粒子在實驗過程中更具有分散性，更能達到修復細胞的效果。由於**本實驗中的MGIPs人參皂苷磁性奈米第五天對受損心肌細胞具有修復效果**，可以應用於修復心肌藥物等領域，以**天然藥物治療無抗藥性**。

參考文獻

- [1] Mei-Hwa Lee*, James L. Thomas, Chun-Lin Liao, Stipo Jurcevic, Tatjana Crnogorac-Jurcevic, Hung-Yin Lin, "Epitope recognition of peptide-imprinted polymers for Regenerating protein 1 (REG1)", Separation and Purification Technology, vol. 192, pp. 213-219, 2018,02.
- [2] Mei-Hwa Lee, James L. Thomas, Chun-Lin Liao, Stipo Jurcevic, Tatjana Crnogorac-Jurcevic, Hung-Yin Lin*, "Polymers imprinted with three REG1B peptides for electrochemical determination of Regenerating Protein 1B,a urinary biomarker for pancreatic ductal adenocarcinoma", Microchimica Acta, vol. 184, no. 6, pp. 1773-1780, 2017,06

靜電紡絲製備矽鈦基奈米纖維其配比變化對形貌及性質之影響



賴佑任 *鍾卓良 紀詠翔 何婕瑜 蘇行一

摘要

在本實驗中，添加酒精、DMF、聚乙烯吡咯烷酮（PVP，1,300,000 Mw）、以TEOS 作為前驅物溶液，將溶液以磁石加熱攪拌機攪拌直至溶液充分混合無沉澱後，於後驅物加入鈦酸四丁酯及鹽酸攪拌至充分混合，放置於高溫爐進行熱處理以 400℃溫度來製備矽鈦基奈米纖維。通過掃描式電子顯微鏡和接觸角測試儀對熱處理後矽鈦基奈米纖維特性進行觀察分析。

實驗結果表明，在以TEOS 為矽源添加的矽鈦基樣品於熱處理後整體能維持其纖維狀，矽鈦基結構的樣品隨著配比不同纖維由平均363.73nm 至 64.8 nm，由最後結果可得知其 TEOS 矽源均勻分散其親水性效果提升，本實驗以 TEOS 作為矽源的有效添加可在未來自潔材料及光觸媒建材等作為應用。

實驗流程

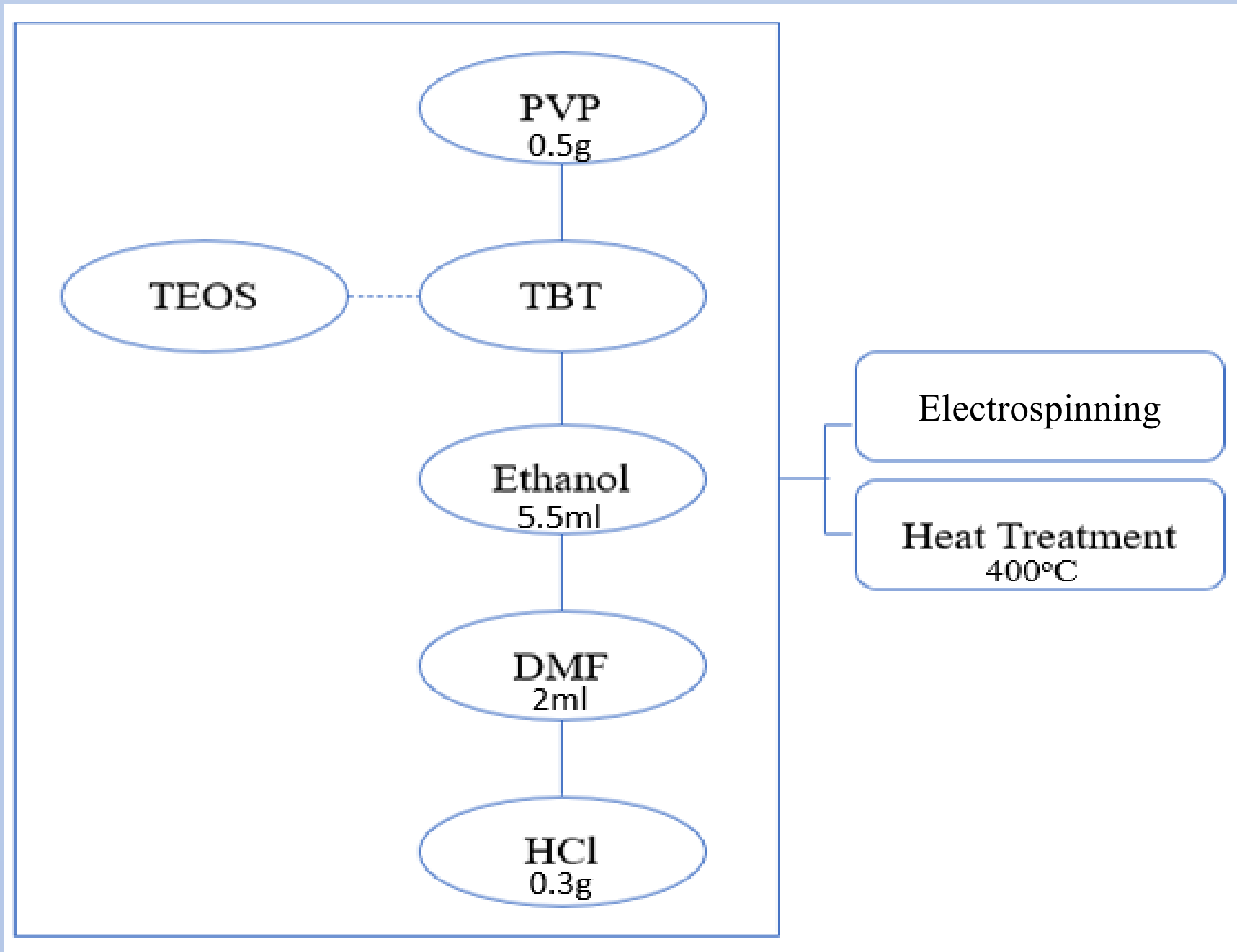
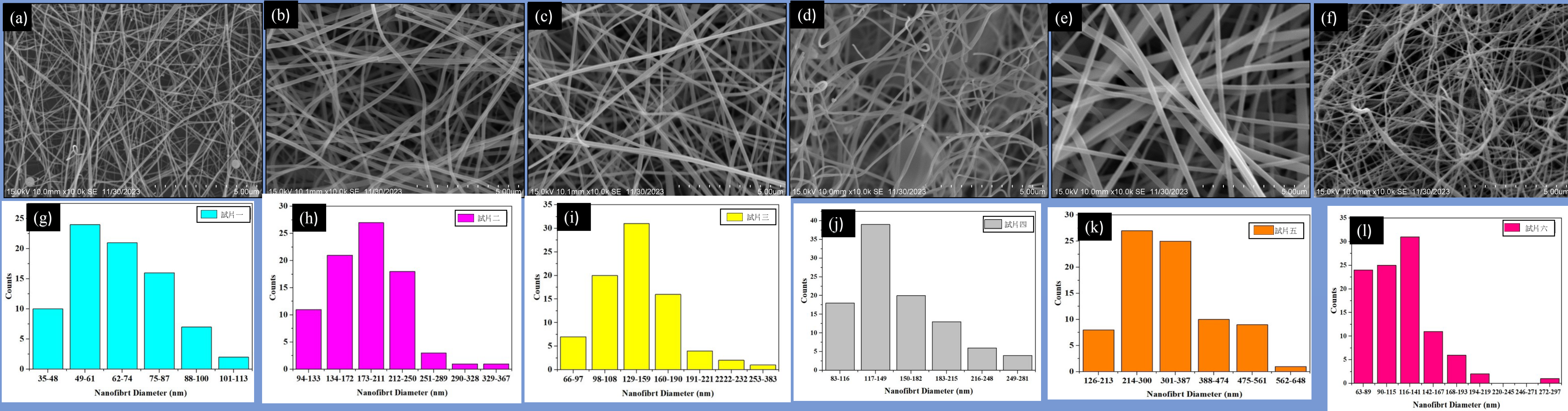


圖1. 靜電紡絲實驗流程圖

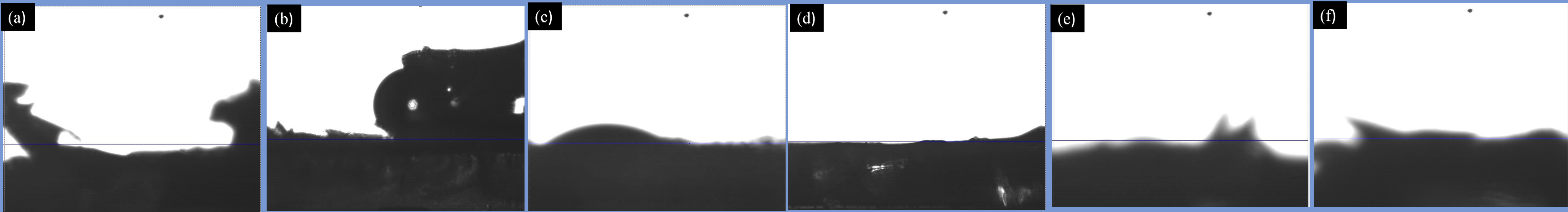
表1. 靜電紡絲矽鈦基奈米纖維配藥表

	TBT (g)	TEOS (g)	流速 (ml/min)
Sample1	0.9	0.5	0.01
Sample2	0.9	0.3	0.01
Sample3	0.6	0.3	0.02
Sample4	0.6	0.5	0.02
Sample5	0.9	0.5	0.02
Sample6	0.6	0.5	0.01

結果與討論



SEM圖及纖維直徑分布圖(a)Sample1 (b)Sample 2 (c)Sample 3 (d)Sample 4 (e)Sample 5 (f)Sample 6 (g) Sample1 平均62.288nm (h) Sample 2 平均184.41nm (i) Sample 3 平均154.31nm (j) Sample 4 平均153.24nm (k) Sample 5 平均330.525nm (l) Sample 6 平均142.57nm



Contact angle (a)Sample1 50.93 ° (b)Sample2 61.68 ° (c)Sample3 25.87 ° (d)Sample4 0 ° (e)Sample5 0 ° (f)Sample6 0 °

結論

- ◆ 該矽鈦基奈米材料屬於一種親水材料，甚至是超親水材料。
- ◆ 矽鈦基奈米纖維直徑會受到流速大小而變粗。
- ◆ 在試片四和試片六可看到纖維末段明顯變細變小，推估原因可能是由於TBT為0.6g，水解出較少的鈦基，導致纖維末端變細。
- ◆ 在固定TBT和流速情況下，會因為TEOS多寡，導致水滴角度有所不同，進而影響親水效果，如試片一和試片六。
- ◆ 在試片一因為流速較小纖維直徑僅有62.28nm，及試片五流速較快直徑約有330.52nm。

Abstract

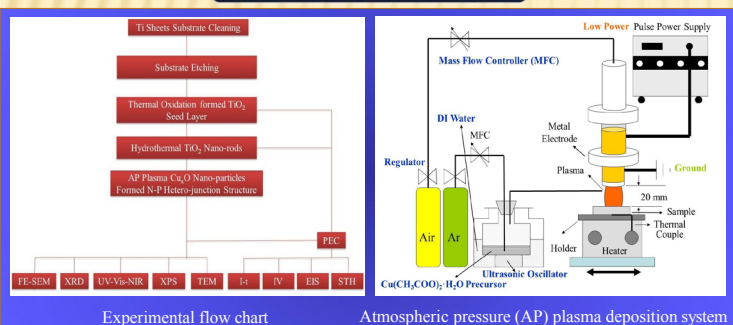
The study adopted the hydrothermal method to prepare TiO_2 nanorods (NRs) regarded as the first layer (N-type semi-conductor) of hetero-structures. Their micro-structure and optoelectronic properties were also investigated. The hydrothermal process involved five process parameters: time, temperature, hydrochloric-acid concentration, precursor concentration and substrate placement direction. The high temperature heat treatment enabled the NRs to become suitable for coating Cu_xO particles. Additionally, the solar to hydrogen (STH) conversion efficiency of TiO_2 NRs was 0.0125% at 0.6 V (vs. RHE). To improve the photo-electrochemical (PEC) hydrogen production efficiency of TiO_2 NRs, Cu_xO particles were used as the second layer (P-type semiconductor) of the hetero-structures. Cu_xO was deposited on the TiO_2 NRs using an atmospheric-pressure plasma jet system. N-P hetero-structures were finally formed, achieving the higher PEC hydrogen production performance. The STH conversion efficiency of the $\text{Cu}_x\text{O}/\text{TiO}_2$ NRs hetero-junction was 0.025% at 0.6 V (vs. RHE), 2 times higher than that of TiO_2 NRs. FE-SEM, XRD, TEM, XPS, UV-Vis, EIS are used to perform morphology, microstructural, chemical bonding, transmission, energy gap and impedance analyses. The solar simulator, three-electrode chemical station and gas chromatograph are used to access the hydrogen production efficiency of the PEC system.

Keywords: Titanium dioxide, Copper oxide, Atmospheric-pressure plasma, Hydrothermal, Photo-electrochemical hydrogen production

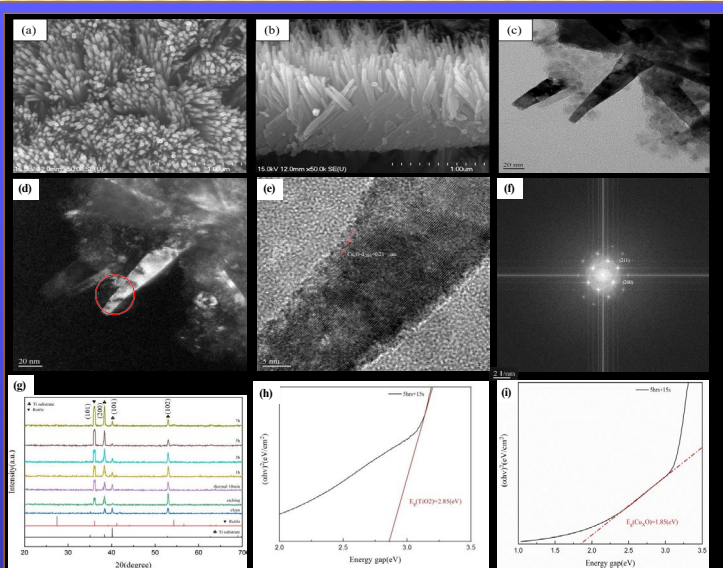
Introduction

The photocatalytic performance of TiO_2 can only be achieved under UV irradiation and its high energy gap limits its application. Therefore, the method to improve the photocatalytic performance of titanium dioxide is to combine it with other low energy gap semiconductor materials (such as cuprous oxide). Titanium dioxide and copper oxide form a composite structure, which can improve the photo-response range and solar energy utilization, and form a heterojunction (NP) with titanium dioxide, its internal electric field can promote effective charge transfer and separation, and inhibit the charge recombination rate, so it can improve its photoelectrochemical (PEC) performance.

Experimental

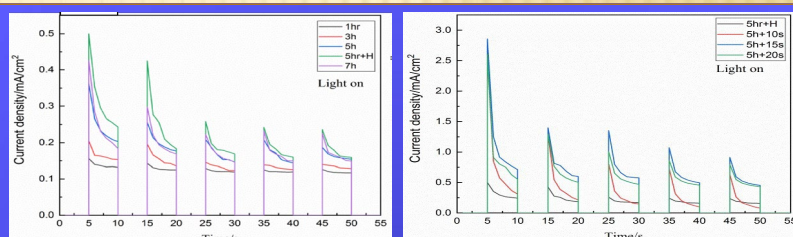


Results and Discussion

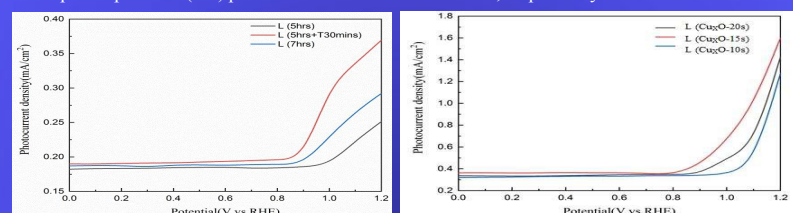


TiO_2 NRs structure synthesized by hydrothermal method (a) Top-view SEM at 5 hrs, (b) Cross-sectional SEM at 5 hrs, (c) TEM for the bright field, (d) TEM for the dark field, (e) HRTEM, (f) Diffraction pattern; (g) XRD pattern of different parameters, (h) The values of TiO_2 and (i) Cu_xO energy gap (Eg) calculated from UV-Vis-NIR analysis.

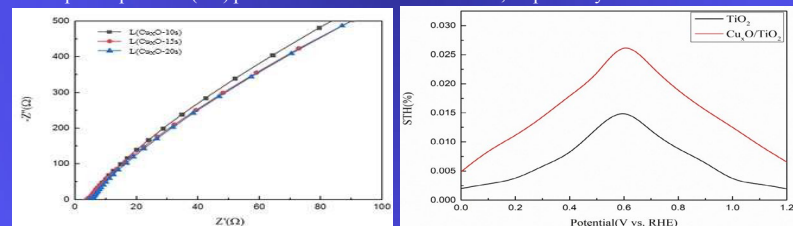
Results and Discussion



I-t curves of (a) TiO_2 and (b) $\text{TiO}_2/\text{Cu}_x\text{O}$ NRs structure synthesized by hydrothermal and atmospheric pressure (AP) plasma methods at different times, respectively.



I-V curves of (a) TiO_2 and (b) $\text{TiO}_2/\text{Cu}_x\text{O}$ NRs structure synthesized by hydrothermal and atmospheric pressure (AP) plasma methods at different times, respectively.



EIS curves of $\text{TiO}_2/\text{Cu}_x\text{O}$ NRs at different times and STH analysis for different structures.

TiO_2 Nano-Rods (NRs)		Solar-to-hydrogen (STH)
TiO_2 (NRs)		0.051%
TiO_2 (NRs)		0.022%
TiO_2 (NRs)		0.015%
Heterojunction		Solar-to-hydrogen (STH)
$\text{Cu}_2\text{O}/\text{TiO}_2$ (NRs)		0.250%
$\text{Cu}_2\text{O}/\text{TiO}_2$ (NRs)		0.100%
$\text{Cu}_2\text{O}/\text{TiO}_2$ (NRs)		0.025%

Comparison of STH at 0 V (vs. RHE)

TiO_2 NRs and $\text{Cu}_x\text{O}/\text{TiO}_2$ N-P hetero-structure

Conclusions

In this study, the hydrothermal process was used to grow titanium dioxide nano-rods as the first layer of the hetero-structure, followed by the use of atmospheric pressure plasma jet system to assist chemical vapor deposition, and copper acetate precursor solution for ultrasonic vibration, and produced Copper oxide particles were successfully plated on nano-rods to form a double-layer hetero-structure. The hetero-junction of copper oxide particles/titanium dioxide nano-rods shows good PEC performance from the analysis of solar hydrogen conversion efficiency and photo-electric test.

Acknowledgment

We thank to the National Science and Technology Council (NSTC 111-NU-E-214-001-NU & NSTC 112-NU-E-214-001-NU) for financial support, and acknowledge to Mrs. Lian-gzhu Wang (TEM operator of National Sun Yat-sen University), Mr. Kun-Shu Li (XRD operator of National Cheng Kung University) and Mr. Ruci-Chin Li (XPS operator of National Cheng Kung University) for their great assistances.