

計畫編號：BN05-00

計畫名稱：尖端材料介面特性在奈米尺度下之分析與操控

計畫主持人：陳正弦

計畫摘要(中)：

在第一期台灣大學優勢重點拔尖計劃之支助下，我們成功的發展一種尖端的微觀能譜顯微分析技術並同時也研發出許多新穎、具有應用價值的奈米材料。兩年來我們的研究團隊已累積豐富的研究能量與專長，我們已準備好挑戰更高難度的研究課題。在此第二期研究拔尖計劃裡，我們鎖定具有高度重要性的新穎奈米材料之界面結構及其電子特性分析為主題。精確的介面研究，長期以來一直是實驗材料科學領域裡一個非常困難的問題。解決此問題一個重要的關鍵，在於是否能從實驗上同時取得具有原子級解析度之介面晶體結構及其電子特性。近年來我們所發展的尖端微觀能譜顯微分析技術—掃描穿透式電子顯微鏡結合電子損失能譜—便是達到此目的一個最有效的實驗技術。本計劃整合了凝態科學研究中心研究人員之專長，針對數種新穎的奈米材料介面進行深入的探討，深信必能在學術拔尖與科技突破方面作出令人矚目的貢獻。

計畫摘要(英)：

In continuation of our existing Excellent Research project which is focused primarily on the development advanced spectro-microscopy techniques and functional complex materials, we propose in this new proposal the studies of interface control and characterizations of advanced functional materials with nanoscale analysis using advanced techniques of spectro-microscopy and theoretical simulations. The simultaneous investigation of structural and electronic information with atomic resolution in the vicinity of interfaces holds the key to unravel the complexities at the interface, and this can only be achieved by techniques that combine capabilities of microscopy and spectroscopy with atomic spatial resolution. The technical expertise of scanning transmission electron microscopy (STEM) and electron energy-loss spectroscopy (EELS) we have developed and excelled recently possesses such a unique combined capability. This main project integrates the core competencies of the Center for Condensed Matter Sciences (CCMS) and comprises six

sub-projects propounded by our faculty members, which cover various aspects of interfaces in diverse materials systems with both scientific and technological significance. Successful interface research requires interdisciplinary technical expertise and CCMS at National Taiwan University is well positioned to make significant contributions in this challenging area.

計畫編號：BN05-01

計畫名稱：低維度奈米材料於能源之應用：介面物理與化學

計畫主持人：林麗瓊

計畫摘要(中)：

本計畫乃建立在前次兩年期計畫所累積之資源與經驗，以本團隊所擅長的奈米材料系統為基礎，靈活應用各種氣相沉積法或分子合成技術，來製備多樣化的複合系統，以適合於新興能源(含太陽能與電化學兩大類)之應用。雖然涵蓋應用面很廣，但我們打算針對一些共通議題作重點研究：(1)複合奈米材料成長機制；(2)表面/介面改質與功能化；(3)表面/介面結構與鍵結分析如 X 光電子能譜與電子損失能譜等；(4) 奈米能源系統之電化學阻抗分析暨其微區分析技術之開發；(5)時析與奈米尺度之激子動態研究；(6)設計由尺寸與表面/介面效應增強之新穎能源元件。針對不同之應用，所須考慮的介面可能包含固態-固態、固態-液態、有機-無機等等。研究這些介面間的電荷分離、傳導與能量轉移現象，並了解表面/介面改質與功能化之後的影響，將有助於我們提昇奈米材料系統產生電力的效能。

計畫摘要(英)：

Building on our previous Excellent Research Project, a number of photovoltaic and electrochemical devices that utilize low-dimensional nanomaterials, including C60 derivatives, carbon nanotubes, semiconductor nanowires and metal nanoparticles, as their key components will be developed. Hybrids of inorganic materials with conjugated polymers, such as PCBM and P3HT, will also be investigated. Nano-structured system with well-controlled interface that either giving better catalytic activity and subsequent current carrier conduction or blending photoactive donor and acceptor plays a decisive role in fabricating high-efficiency electrochemical or solar cells, respectively.

Our main emphases will be placed on (1) study of the energetic and formation kinetics of these nanostructures and their composites; (2) functionalization of the surface of these nanostructures and their interface properties; (3) analysis of the interface/surface structure and physical/chemical property in nanoscale; (4) spectroscopic studies using two-color pump-probe transient absorption spectroscopy for the energy relaxation and dissociation dynamics of the photoinduced excitons; (5) tera-Hertz spectroscopy for non-contact mobility and polarization measurements in photovoltaic systems to determine the genuine steady-state electrical properties of exciton and polaron; and (6) Designing “smart” micro-devices with interface-controlled properties.

計畫編號：BN05-02

計畫名稱：功能性氧化物介面之操控及其相關物理

計畫主持人：林昭吟

計畫摘要(中)：

鈣鈦礦展現了豐富的磁和電的性質。其性質取決於它們的結構和化學的成分。因此、結合不同的鈣鈦礦氧化物系統，或是金屬/鈣鈦礦氧化物的介面形成產生了一個新的研究領域。特別是不同鈣鈦礦氧化物介面或超晶格的介面性質可以促成一些獨特的功能性元件。例如，鈣鈦礦電阻式隨機記憶體元件的介面控制了電阻轉換量的大小；而錳氧化合物的磁性也可在與超導體結合的介面上透過鄰近效應改變其超導性。在這個子計劃裡，我們運用了已經有的脈衝雷射蒸鍍系統，並結合反射高能電子繞射儀去製作原子級平整的鈣鈦礦氧化物雙層膜，包括各種不同載流子的錳氧化物。藉由改變介面電子態，去改質並研究氧化物/氧化物及氧化物/金屬的介面的物理性質。

計畫摘要(英)：

Perovskite oxides show rich magnetic and electrical properties [1-3], depending on their lattice structure and chemical compositions. Thus, the combination of different Perovskite oxide systems, or the interface of metal/Perovskite-oxide generates a new area of extensive studies. In particular, the interface properties of the various oxide junctions and superlattices are important for producing the novel functional devices. For example, the interface of Perovskite Resistance Random Access

Memory (RRAM) device controls the magnitude of resistive switching and the magnetism of manganite can also change the superconductivity at the interface due to the proximity effect. In this sub-project, we use the existing pulsed-laser-deposition (PLD) system in combining the reflection-high-energy-electron-diffraction (RHEED) system to fabricate the atomic flat bilayers of perovskite oxides, including various manganites with different carrier concentration. By changing the interface electronic structure to engineer/study their properties of metal/oxide and oxide/oxide interfaces.

計畫編號：BN05-04

計畫名稱：利用射頻掃瞄穿隧顯微鏡研究原子分子動態行為及電子自旋共振

計畫主持人：白偉武

計畫摘要(中)：

本計畫將建立射頻掃瞄電流穿隧顯微鏡技術(RF-STM)。基本方法是利用阻抗轉換匹配電路的反射來快速偵測穿隧電阻的變化，見參考資料「1」。這個技術可將掃瞄電流穿隧顯微鏡的時間解析度容易的提升到微秒級。另外，此技術也可以提升偵測原子級尺度下的電子動態現象的靈敏度，如電子自旋共振 (ESR)。本計畫的目標可分為儀器研製以及基礎研究。在儀器研製方面，我們將設立臺灣第一套 RF-STM。此外，我們將拓展此技術，如加入共振 Q 值的控制和利用射頻反射功率作為顯像的回饋信號。第一年內，將把射頻偵測線路與現有的一台大氣 STM 整合起來，測試顯像及偵測穩定自由基在石墨上的電子自旋共振信號。第二，三年內，我們將把 RF—STM 與超高真空（及低溫，若條件許可）環境結合，以在調控的環境下研究表面及介面行為。在基礎研究方面，我們將研究兩個課題：(1) 偵測原子或分子在表面或介面的動態行為。(2) 偵測電子自旋共振。在第一個課題上，我們將研究在 C60 與銀(100)面之間，介面結構瞬時的變化。這對以往無法以顯微方法研究分子薄膜之下的原子運動可以提供新的理解。另外也研究 NCH₃/Cu(110) 和 O/Ag(110) 系統。在第二個課題上，我們將研究內包氮原子的碳六十(N@C60)和 NaCoO₂。N@C60 有一穩定的順磁電子自旋，是適當的樣品，也可同時改變碳六十的電荷來觀察自旋行為的變化。NaCoO₂ 是目前凝態物理內一個相當熱門的材料，因為此材料與自旋受挫，量子臨界點，金屬—絕緣

相變等相關。我們目前是全球唯一成功得到此材料表面 STM 顯像的研究組，相信利用 RF-STM，有潛力得到此材料的微觀自旋結構，並探討其與原子結構的關連性。

計畫摘要(英)：

In this proposal, we will develop radio-frequency scanning tunneling microscopy (RF-STM). The basic idea is to use reflection from an impedance transformation resonant RF tank to rapidly sense the tunneling junction resistance, as outlined in ref. [1]. This technique easily extends the temporal resolution of STM to μs scale. Furthermore, it provides a possibility to study atomic-scale dynamics of electronic phenomena, e.g., electron spin resonance, with enhanced sensitivity. Our goal is two-fold. Instrument-wise, we will build the first RF-STM in Taiwan. In addition, we will extend this technique by adding Q-control of impedance matching network and use RF power as feedback signal for imaging. In the first year, RF-STM will be constructed on an existing ambient STM. We will test its imaging capability and also detect ESR signal of stable radicals on HOPG. In later years, the RF-STM setup will be adapted to ultrahigh vacuum and preferably low temperature (e.g., ~ 5 K) environment to study surface and interface phenomena under well-defined condition. Science-wise, we focus on two subjects: (1) detection of fast transit motion of atoms or molecules at surface or interface, and (2) detection of electron spin resonance (ESR) of a single spin. For the former subject, fast transient structure reorganization at the C60/Ag(100) interface will be studied. This sheds light on the important issue of atom transport underneath molecular adlayer that has not been studied before. Two other systems, NCH₃/Cu(110) and O/Ag(110) are also of interest. For the latter subject, we will study endohedral N@C60 and Na_xCoO₂. N@C60 has a long-lived paramagnetic spin. We also plan to study spin resonance as the C60 cage charge state is varied. In Na_xCoO₂, the connection between Na ordering and spin structure will be studied. Na_xCoO₂ is a material in which several hot issues such as quantum frustration of electron spins, possible quantum criticality, metal-insulator transition etc, all come into play. We are so far the only group that succeeds in imaging Na_xCoO₂ surface with STM. RF-STM

has the exciting potential of obtaining direct real-space view of spin structure in this material.

計畫編號：BN05-05

計畫名稱：掃描穿透式電子顯微鏡結合電子損失能譜：原子級解析度之介面晶體與電子結構分析

計畫主持人：朱明文

計畫摘要(中)：

氧化物異質介面(complex oxide heterostructures)以其截然不同於塊材(bulk)的物理及化學特性，成為在科學研究領域中一直備受關注的一支。一般而言，人們咸信介面附近之應變(strains)、化學鍵結、成分、元素價數、及結構缺陷是造成此一與塊材相異性的主要來源，然而，這些可能性一直缺乏直接證據的支持。為徹底了解上述可能性對介面特性的真正影響，非得要直接研究介面附近的原子層(atomic columns)之結構及電子性質不可，且這樣的研究只有同時兼備原子級(atomic resolution)影像觀察(microscopic)及光譜(spectroscopic)的研究工具才可達到。掃描穿透式電子顯微鏡(scanning transmission electron microscopy)結合電子損失能譜儀(electron energy-loss spectroscopy)，是現有的研究工具中唯一一個可以達到此目的的技術。在本中心建構掃描穿透式電子顯微鏡結合電子損失能譜儀並應用於由林昭吟團隊所製備之氧化物異質介面研究(子計畫二)便是本計畫的中心思想。

計畫摘要(英)：

Interfaces in complex oxide heterostructures exhibit as a fertile ground of scientific researches, because the physical and chemical characteristics they display can be drastically different from those in bulks. The effects of interfacial strains, chemical variations (such as bonding features, compositions, and elemental valences), and/or structural defects are believed to account for such distinct properties at the interfaces, whereas a direct evidence is generally missing. To unravel this puzzle, a simultaneous investigation of structural, electronic information of the atomic columns in the vicinity of interfaces is indispensable, and can only be achieved by techniques that combine microscopic and spectroscopic capabilities with atomic resolution. Scanning transmission electron microscopy (STEM) in conjunction with

electron energy-loss spectroscopy (EELS) is the only existing technique showing such a combined capability. The objective of this proposal is to establish this unmatched STEM-EELS technique designed for characterizations of core-level excitations which reflect rich information of bonding in materials in house, and apply it to investigations of the oxide interfaces prepared by the group of Dr. J. G. Lin (Sub-Proposal 2).

計畫編號：BN05-06

計畫名稱：異質介面之物化性質的理論計算研究

計畫主持人：林倫年

計畫摘要(中)：

我們希望開發並建立一套實用的量子化學/物理計算方法，為不同介面的物化性質研究提供第一原理等級的計算。本計畫也預期能為此整合計畫中與實驗相關的分項計畫提供計算協助與理論層次解釋。同時也將提供學生、研究助理、博士後研究員、以及研究員們一個如何應用最新的量子化學/物理計算技巧的學習機會。

在實作上，我們將會集中於以下三個主題上：

(1) 材料表面缺陷對吸附機構與化學活性的影響

最近，實驗發現到由乙醇轉化成氫氣的反應在 CeO_2 表面上具有十分顯著的效益。同時，研究也發現表面缺陷的位置(氧的空缺處)可能對此高效率反應扮演著十分重要的角色，這是可能是因為 4-f 軌域的電子被帶走而形成 Ce^{3+} 。但這對傳統化學直覺來說是件極具爭議的結論，因為 4-f 電子是十分定域化的，同時其最大出現機率是被發現在比波爾半徑更小的距離內。因此，研究具有 4-f 或 5-f 電子金屬氧化物化學性質與應用的第一要務，就是解釋在吸附程序或化學反應中 4-f 電子所扮演的角色。希望藉由本計畫能闡明各種形式的表面缺陷對吸附機制與化學反應的影響。

(2) 延展系統吸附大分子的電子激發態

最近時間相關密度泛函數理論的應用已經可以成功計算部分大分子系統的一些光學性質。為了預測有限系統的激發態幾何結構，TD-DFT 方法發展出數值梯度計算程序，因此可以建構出電子激發態的位能表面。借助新的 TD-DFT 技術，我們希望能夠有系統地研究分子與不同尺寸的奈米團簇間作用的激發態性質，特別是幾何結構的改變。

(3) 具有大量區域穩定結構系統的能量以及原子與分子轉移的理論

模擬

在計算化學與物理領域裡眾所皆知的是：對於大尺度體系來說，全域幾何結構最佳化是個相當大的問題，這是因為在些微能量差異下，存在著相當大量的異構物，要闡釋所有可能的幾何構型可以說是不可可能的。因此我們想要進行一項大膽的嘗試，提出兩個途徑來處理這樣的問題：(a) 使用較為簡單的理論模型來取代第一原理計算；以及(b) 利用第一原理計算方法所得的結果來建立適合的動態蒙地卡羅(Kinetic Monte Carlo)模擬的參數。在此主題中，我們將對水分子系統、金屬合金團簇、以及表面分子吸附作為研究主軸

計畫摘要(英)：

We would like to develop and establish feasible quantum chemistry/physics calculation approaches for the studies of chemical and physical properties on heterogeneous interfaces using the first principle calculation methods. This project is also intended to provide computational supports and theoretical interpretations to experimental results from other projects proposed in the main project. We will also provides students, research assistants, post doc fellows, and research fellows with a number of opportunities to learn how to apply the-state-of-the art quantum physics/chemistry calculation techniques.

In particular, we would like to focus on the following three subjects:
(1) The effects of defects of the surface of extended systems on adsorption mechanisms and chemical reactivities.

Quite recently, it is experimentally found that the conversion of ethanol to H₂ is quite remarkably efficient on CeO₂ surface and it is suggested that defect sites (or oxygen vacancy sites) may play an important role on the high efficiency because oxygen vacancy may lead to Ce³⁺ that bears one electron in one of the 4-f orbitals. It is very controversial from conventional chemical intuition (or wisdom) because a 4-f electron is quite localized on the atomic site and the most probable distribution finding an electron in 4-f orbitals occurs at a shorter distance than the Bohr radius. Therefore elucidation of a role of 4-f electron on adsorption processes or chemical reactions is the primary issue in studying chemical properties and applications of the metal oxides that contain 4-f or 5-f electrons. In this subject, we would like to shed light on

effects of various types of defects of surfaces on adsorption mechanisms and chemical reactions.

(2) Electronically excited states of large molecular systems adsorbed on extended systems.

Recently time-dependent density functional theory (TD-DFT) has made it partially possible to compute some of the optical properties of relatively large molecular systems. TD-DFT method has just been explored to predict the geometry of excited states of finite systems using numerical gradient calculation scheme, which allows constructing potential surfaces of the electronically excited states. With the new TD-DFT technique, we would like to systematically investigate the excited state properties of a molecule interacting with a nano-cluster as a function of the cluster size, especially for the geometrical changes.

Theoretical modeling of energy and/or atom and molecule transfers in a system in which a vast number of local minima exist.

It has been recognized in the computational chemistry and physics communities that global optimization of the geometry of a large system is quite a problem because there may exist a number of “isomers” with slightly different energies. Elucidation of all possible geometrical configurations is, therefore, practically impossible. Therefore we would like to make a bold attempt, proposing two approaches for this problem: (a) a rather simple theoretical modeling instead of a direct application of first principle calculation; and (b) adaptive Kinetic Monte Carlo simulation based on the parameters obtained using first principle calculation methods. For this subject, water systems, metal alloy clusters, a molecule adsorbed on surface are of particular interest.