行政院國家科學委員會專題研究計畫　成果報告

一維奈米材料與氣相自由基離子之製備及光譜特性研究

計畫類別：個別型計畫
計畫編號：NSC92-2113-M-002-039-
執行期間：92年08月01日至93年10月31日
執行單位：國立臺灣大學化學系暨研究所

計畫主持人：陳逸聰

計畫參與人員：Rayapati Venugopal（博士後研究員），楊逸涵（博士生），吳幸臻（博士生），於平（博士生），邱慧珊（碩士生），莊啟宏（碩士生），劉仲展（碩士生），張英德（碩士生）。

報告類型：精簡報告
報告附件：出席國際會議研究心得報告及發表論文
處理方式：本計畫可公開查詢

中　華　民　國 94年5月18日

行政院國家科學委員會補助專題研究計畫成果報告

計畫名稱：一維奈米材料與氣相自由基離子之製備及光譜特性研究

計畫類別：■ **個別型計畫**　　□ **整合型計畫**
計畫編號：NSC 92-2113-M-002-039
執行期間：92 **年** 8 **月** 1 **日至** 93 **年** 10 **月** 31 **日**

計畫主持人：陳逸聰
共同主持人：
計畫參與人員：

Rayapati Venugopal **（博士後研究員），楊逸涵（博士生），吳幸臻（博士生），於平（博士生），邱慧珊（碩士生），莊啟宏（碩士生），劉仲展（碩士生），張英德（碩士生）。**

成果報告類型(依經費核定清單規定繳交)：■**精簡報告**　□**完整報告**

本成果報告包括以下應繳交之附件：
□**赴國外出差或研習心得報告一份**
□**赴大陸地區出差或研習心得報告一份**
□**出席國際學術會議心得報告及發表之論文各一份**
□**國際合作研究計畫國外研究報告書一份**

執行單位：國立臺灣大學化學系暨研究所

中　華　民　國 94 **年** 5 **月** 18 **日**

一．中文摘要

我們以多光子共振游離光譜（REMPI）的技術研究溴乙烯、丙二烯與硫甲醛分子的高雷德堡能態。在溴乙烯分子的研究方面，70000 到 80000 cm^{-1} 的能量範圍之間，得到了一組 s、三組 p、兩組 d 和一組 f 等七組雷德堡系列，並藉由雷德堡公式的回歸分析，得到溴乙烯分子的游離能為 79194 ± 17 cm^{-1} (9.819 ± 0.002 eV)。丙二烯在 56500 到 85000 cm^{-1} 之間的 2+1 REMPI 光譜，顯示了密集的譜線特徵，經分析指認確認為 p*? p、3p? p、4s? p、4p? p、4d? p 等躍遷。光譜的分析指認與 *ab initio* 分子軌域及時間相依密度泛函數理論的計算結果相當一致。另外，我們也觀察到在一些電子激發態中，CH_2 扭曲振動態(?$_4$ ~770 cm^{-1})有振動系列的出現，藉由 Franck-Condon 因子的計算結果，亦可確認 CH_2 扭曲振動態是躍遷強度較大的振動模式。在硫甲醛分子的研究方面，我們以雙共振增強三光子游離光譜(DRETPI)的技術，研究硫甲醛的電子-振動激發態。硫甲醛分子的 $\tilde{C}$ ($^1B_2$)電子激發態作為雙共振激發過程的中間態，再激發至 62000 到 72000 cm^{-1} 之間的高雷德堡態。比較單光子吸收與 DRETPI 躍遷，分別由 $\tilde{X}$ ($^1A_1$)與 $\tilde{C}$ ($^1B_2$)作躍遷，利用光譜的選擇律，可以分析辨認出一組價電子態(np, p*^{2})躍遷與十組雷得堡態(n, 5s)、(n, 5p$_z$)、(n, 5p$_x$)、(n, 5p$_y$)、(n, 4d$_{z^2}$)、(n, 4p$_{xz}$)、(n, 4d$_{yz}$)、(n, 6s)、(p, 4p$_y$)、(n, 6p$_x$)出現在 DRETPI 的光譜中。

以 M^{2+}/kaolin（M = Fe, Co, Ni, Cu）作為催化劑，利用 CCVD 的方法，可以大量合成直徑約 400 到 2000 nm 之間的碳球。碳球的結構是由未封閉的石墨層所組成，層與層之間的距離為 0.33–0.35 nm 左右，這種石墨層狀結構使得碳球在 80 °C 的過錳酸鉀(H$^+$)溶液中仍具有活性，在氟化氫（48%）溶液中維持穩定狀態。我們以雷射剝蝕法的幫助，金屬與二氧化矽的催化作用下，合成矽奈米線繩。以純金屬作為催化劑（Fe, Ru, Pr）時，所生成的單晶結構矽奈米線繩具有一穩定的晶面{111}，且矽奈米線繩的生長是沿著<111>的方向，其生長機制是遵循 VLS 的過程，所合成出的矽奈米線繩，其尖端具有一金屬頭，是由金屬和矽所組成($FeSi_2$, $RuSi_3$, $PrSi_4$)。相對地，以二氧化矽作為催化劑時，所合成出的矽奈米線繩，其晶體的晶面成長軸向為<111>，奈米線繩的成長方向則為<112>，以二氧化矽催化所生長的矽奈米線繩末端沒有頭的存在。以表面增強拉曼散射研究二氧化鈦奈米粒子，對沉積於粗糙金表面的 polypyrrole 分子的影響，粗糙的金表面基材是以電化學方法以氧化還原的循環過程，使金表面在 0.1 N 的鹽酸水溶液中進行粗糙化，水溶液中含有 1 mM rutile 結構的二氧化鈦奈米粒子，過程中並以紫外光源進行照射。實驗的結果顯示，在陽極掃描過程發現氧化峰的訊號有明顯地增強，其原因來自所添加的二氧化鈦在電場與紫外光的幫助下，使得表面增強拉曼散射的效應顯現。這些沉積在粗糙金表面的 polypyrrole 分子，其拉曼訊號在有二氧化鈦的存在下，訊號增強了有 5 倍之多。以化學氣相沉積法及雷射剝蝕的幫助，我們合成了單晶結構的硒化鎘奈米帶與奈米薄片。硒化鎘的奈米結構為六方 wurtzite，奈米帶的長度在幾十個微米到一百微米之間，厚度在 40 到 70 nm 左右，寬度由一端為 3 μm，逐漸縮小至另一端約為 100 nm 大小，在較細的一端具有一金奈米粒子，為硒化鎘的成長催化劑。硒化鎘奈米帶的成長機制為 VLS 與 VS 兩種方式的組合，而奈米薄片的成

長機制則是以 VS 的過程為主。另外，我們以表面增強拉曼散射光譜測量硒化鎘奈米帶的聲子振動模，並以非共振與接近共振的兩種光源進行激發。相對於塊材的硒化鎘，奈米帶硒化鎘的縱向光學聲子振動模有藍位移的現象，大小為 2.4 cm^{-1}**，其原因來自於帶狀結構的晶格收縮。同樣與塊材硒化鎘粉末做比較，在室溫下，單一根硒化鎘奈米帶的顯微光致放光位於** 1.74 eV **左右，強度比塊材大了有** 3 **倍之多，而激發光源的偏振方向與硒化鎘奈米帶的放光角度，存在著相對應的關係。**

關鍵字：溴乙烯；丙二烯；硫甲醛；碳球；矽奈米線繩；硒化鎘奈米帶；表面增強拉曼散射；顯微光致放光。

二．Abstract

High-lying Rydberg states of vinyl bromide (C_2H_3Br), allene ($H_2C_3H_2$), and thioformaldehyde (H_2CS) have been investigated by resonance-enhanced multiphoton ionization (REMPI) spectroscopy. In the study of vinyl bromide, seven Rydberg series of 70000–80000 cm^{-1}, including one *s*, three *p*, two *d*, and one *f*, have been identified. With a Rydberg formula fitting to the observed Rydberg series, the ionization energy of 79194 ± 17 cm^{-1} (9.819 ± 0.002 eV) of vinyl bromide has been determined. In the 2+1 REMPI spectra of allene at 56500–85000 cm^{-1}, very congested REMPI spectral features have been assigned as due to $\pi^*\leftarrow\pi$, $3p\leftarrow\pi$, $4s\leftarrow\pi$, $4p\leftarrow\pi$, and $4d\leftarrow\pi$ transitions. The spectroscopic assignments were facilitated with *ab initio* MO and time-dependent density functional theoretical calculations. CH_2 twisting (ν_4 ~770 cm^{-1}) related vibrational progressions have been observed for several excited electronic states and the CH_2 twisting is the most active vibrational mode as confirmed by calculated Franck-Condon factors. Vibronically excited thioformaldehyde has been studied by double-resonance enhanced three-photon ionization (DRETPI) spectroscopy, where the $\tilde{C}(^1B_2)$ state of thioformaldehyde was used as an intermediate for the double-resonance excitation to the high-lying electronic states at 62000–72000 cm^{-1}. In light of distinctive selection rules in the one-photon absorption and DRETPI transitions excited from $\tilde{X}(^1A_1)$ and $\tilde{C}(^1B_2)$, respectively, one valence ($n\pi$, p^{*2}) and ten Rydberg states, (n, $5s$), (n, $5p_z$), (n, $5p_x$), (n, $5p_y$), (n, $4d_z^{\,2}$), (n, $4p_{xz}$), (n, $4d_{yz}$), (n, $6s$), (p, $4p_y$), and (n, $6p_x$) of H_2CS, have been identified in the DRETPI spectrum.

Carbon spheres with diameter of 400–2000 nm were synthesized with the catalyst of M^{2+}/kaolin (M = Fe, Co, Ni, Cu) by CCVD in a large quantity. The carbon spheres are

composed of unclosed graphene layers with 0.33–0.35 nm distance between layers. This kind of unclosed graphitic layer structure makes the carbon spheres active in $KMnO_4$ (H^+) solution at 80°C, but remain stable in HF (48%) solution. Silicon nanowires (SiNWs) have been fabricated with metal- and SiO_2-catalyses assisted by laser ablation. In the catalytic growths of single-crystalline SiNWs by pure metal catalysts (Fe, Ru, and Pr), Si {111} is found to be the most stable plane and wire growth axis is along <111>. The growth mechanism follows a vapor-liquid-solid (VLS) process, and the synthesized SiNWs typically have metal-tips composed of metal and Si, such as $FeSi_2$, $RuSi_3$, and $PrSi_4$, respectively. In sharp contrast, crystalline growth axis of <111> and wire growth axis of <112> are resulted in the SiNWs catalyzed by SiO_2. Besides, the SiO_2-catalytic SiNWs generally have no tips at the wire ends. In the study of effect of TiO_2 nanoparticles on the improved surface-enhanced Raman scattering (SERS) of polypyrrole deposited on roughened gold substrates, electrochemical oxidation-reduction cycle procedure to roughen gold substrates in 0.1 N HCl aqueous solution containing 1 mM rutile TiO_2 nanoparticles under the irradiation of UV light was examined. It is encouraging to find that the oxidized peak in the anodic scan, which is responsible for the SERS, increases significantly due to the effect of adding TiO_2 under an electric field and UV irradiation. Moreover, the SERS spectrum of polypyrrole electrodeposited on the corresponding roughened gold substrate exhibits a 5-fold higher intensity compared to that without the contribution of TiO_2 nanoparticles. Single-crystalline CdSe nanobelts and sheets have been fabricated by a CVD method assisted with laser ablation. The hexagonal wurtzite CdSe nanostructures can range in length from several tens to a hundred of μm, thickness from 40 to 70 nm, and a tapered width which is ~3 μm at one end and tapers off to ~100 nm at a catalytic gold particle. While the growth mechanism of nanobelts complies with a combination of VLS and vapor-solid (VS) processes, the formation of sheets is primarily based on VS mechanism. The phonon modes of CdSe nanobelts have been measured by SERS spectroscopy with off- and near-resonant excitations. A blue-shift of 2.4 cm^{-1} for the longitudinal optical phonon of CdSe nanobelts, relative to bulk CdSe, is attributed to a lattice contraction in the belt structure. Room-temperature micro-photoluminescence at ~1.74 eV from single CdSe nanobelts shows a 3-fold enhancement comparing with that from bulk CdSe powder, and displays a partial polarization dependence of emission angles.

Keywords: vinyl bromide, allene, and thioformaldehyde, carbon spheres, silicon nanowires, cadmium selenide nanobelts, surface-enhanced Raman scattering, micro-photoluminescence

三. Report

In the past academic year, we have focused on the studies of (1) high-lying molecular Rydberg states by multi-photon resonant ionization spectroscopy and (2) growth and spectroscopic characterization of nanoscale materials. The research results and publications are summarized as follows.

1. High-lying molecular Rydberg states by multi-photon resonant ionization spectroscopy

Vinyl bromide (C_2H_3Br)

"High-lying Rydberg states of vinyl bromide studied by two-photon resonant ionization spectroscopy", C.-H. Chuang, C.-C. Chen, H.-C. Wu, and Y.-T. Chen; *Chemical Physics Letters*, **394**, 287-292 (2004).

High-lying Rydberg states of vinyl bromide at 7000–79500 cm^{-1} have been investigated using 2+1 resonance-enhanced multiphoton ionization (REMPI) spectroscopy. Seven Rydberg series, including one *s*, three *p*, two *d*, and one *f*, have been identified from fitting the term values of observed electronic states to Rydberg formula rendering the ionization energy of 79194 ± 17 cm^{-1} (9.819 ± 0.002 eV). All of the seven series converge to the same ionization-energy limit, corresponding to the ground state of vinyl bromide cation. The adiabatic ionization energy of vinyl bromide determined from this study is in excellent agreement with the values reported recently by other methods.

Allene ($H_2C_3H_2$)

"Two-photon vibronic spectroscopy of allene at 7.0-10.5 eV: Experiment and theory", J.-C. Shieh, J.-C. Wu, R. Li, J.-L. Chang, Y.-J. Lin, D.-W. Liao, M. Hayashi, A. M. Mebel, N. C. Handy, and Y.-T. Chen; *Molecular Physics*, **102**, 229-248 (2005).

We have observed 2+1 resonance-enhanced multiphoton ionization (REMPI) spectra of allene at 7.0–10.5 eV. The excited vibronic symmetry has been determined from polarization-ratio measurements. Based on the vibronic energies and peak intensities calculated using *ab initio* MO and time-dependent density functional theory, the very congested REMPI spectra have been assigned as due to $\pi^*\leftarrow\pi$, $3p\leftarrow\pi$, $4s\leftarrow\pi$, $4p\leftarrow\pi$, and

4d←π transitions. Vibrational progressions related to the CH_2 twisting (ν_4 ~770 cm^{-1}) have been observed for several excited electronic states. Calculated Franck-Condon factors also confirm that CH_2 twisting is the most active mode in the vibronic spectra of allene. In this study, we have performed theoretical calculations of two-photon intensities and polarization ratios through the *ab initio* computed one-photon transition dipole moments to various electronic states as intermediates. As a starting point to interpret the complicated vibronic spectrum of allene, the theoretical approach, without vibronic couplings, has been applied to predict the peak positions, spectral intensities, and polarization ratios of Rydberg states, and qualitatively shows a considerable agreement with experimental observations.

Thioformaldehyde (H_2CS)

"Rydberg states of thioformaldehyde at 60000–70000 cm^{-1} studied by two-color resonance enhanced ionization spectroscopy", H.-C. Wu, C.-C. Chen, and Y.-T. Chen; *Journal of Chemical Physics*, submitting (2005).

Vibronically excited thioformaldehyde (H_2CS) has been studied by double-resonance enhanced three-photon ionization (DRETPI) spectroscopy, where the $\tilde{C}(^1B_2)$ state of H_2CS was used as an intermediate for the double-resonance excitation to the high-lying electronic states at 62000–72000 cm^{-1}. The H_2CS molecules were produced by the flash pyrolysis (~700 °C) of trimethylene sulfide in a supersonic-jet expansion. Spectroscopic analysis for the observed vibronic transitions has been facilitated with *ab initio* calculations of electronic excitation energies, oscillator strengths, and Franck-Condon factors. Identified Rydberg states of H_2CS have further been confirmed by their quantum defects rendered from a fitting to Rydberg formula. In light of distinctive selection rules in the one-photon absorption and DRETPI transitions excited from $\tilde{X}(^1A_1)$ and $\tilde{C}(^1B_2)$, respectively, one valence (np, p^{*2}) and ten Rydberg states, (n, $5s$), (n, $5p_z$), (n, $5p_x$), (n, $5p_y$), (n, $4d_z^2$), (n, $4p_{xz}$), (n, $4d_{yz}$), (n, $6s$), (p, $4p_y$), and (n, $6p_x$) of H_2CS, have been identified in the DRETPI spectrum.

2. Growth and spectroscopic characterization of nanoscale materials

Carbon spheres

"Synthesis and properties of carbon nanospheres grown by CVD using Kaolin supported transition metal catalysts", J.-Y. Miao, D. W. Hwang, K. V. Narasimhulu, P.-I. Lin, Y.-T. Chen, S.-H. Lin, and L.-P. Hwang; *Carbon*, **42**, 813-822 (2004).

Carbon spheres with diameter of 400~2000 nm are synthesized with the catalyst of M^{2+}/kaolin (M = Fe, Co, Ni, Cu) by CCVD in a large quantity. More than 90% of the carbon spheres have the sizes of 600~800 nm. The synthetic reaction is carried out at a temperature higher than 650℃ for 1~2 hours. 750~850℃ is a suitable temperature region for the reaction. Reaction gases of N_2 and C_2H_2 can synthesize and separate the carbon spheres at 200 and 50 sccm. The carbon spheres are composed of unclosed graphene layers with 0.33~0.35 nm distance between layers. This kind of unclosed graphitic layer structure makes the carbon spheres active in $KMnO_4$ (H^+) solution at 80℃. However, the carbon spheres remain stable in HF (48%) solution. The carbon spheres can be dissolved in carbon disulfide, 1-methylnaphthalene and 1,2-dichlorobenzene.

Silicon nanowires

"Catalytic growth of silicon nanowires assisted by laser ablation", Y.-H. Yang, S.-J. Wu, H.-S. Chiu, P.-I. Lin, and Y.-T. Chen; *Journal of Physical Chemistry B*, **108**, 846-852 (2004).

Silicon nanowires (SiNWs, dia. $\geq$ 5 nm and length ~ μm) have been fabricated with metal- and SiO_2-catalyses assisted by laser ablation. In the catalytic growths of single-crystalline SiNWs by pure metal catalysts (Fe, Ru, and Pr), Si {111} is found to be the most stable plane and wire growth axis is along <111>. The growth mechanism follows a vapor-liquid-solid process, and the synthesized SiNWs typically have metal-tips composed of metal and Si, such as $FeSi_2$, $RuSi_3$, and $PrSi_4$, respectively. In sharp contrast, crystalline growth axis of <111> and wire growth axis of <112> are resulted in the SiNWs catalyzed by SiO_2. Besides, the SiO_2-catalytic SiNWs generally have no tips at the wire ends. Distinctive growth mechanisms resulting from metal- and SiO_2-catalyses will be discussed. Pressure effect on the longitudinal and transverse growing rates in the fabrication of SiNWs has been examined.

Surface Enhanced Raman Scattering (SERS)

"Effect of TiO_2 nanoparticles on the improved surface-enhanced Raman scattering of polypyrrole deposited on roughened gold substrates", Y.-C. Liu, P.-I. Lin, Y.-T. Chen, M.-D. Ger, K.-L. Lan, and C.-L. Lin; *Journal of Physical Chemistry B*, **108**, 14897-14900 (2004).

We reported the first electrochemical oxidation-reduction cycle procedure to roughen gold substrates in 0.1 N HCl aqueous solution containing 1 mM rutile TiO_2 nanoparticles under the irradiation of UV light. It is encouraging to find that the oxidized peak in the anodic scan, which is responsible for the SERS, increases significantly due to the effect of adding TiO_2 under an electric field and UV irradiation. Moreover, the SERS spectrum of polypyrrole electrodeposited on the corresponding roughened gold substrate exhibits a 5-fold higher intensity compared to that without the contribution of TiO_2 nanoparticles.

CdSe nanobelts and nanosheets

"Surface enhanced Raman scattering and polarized photoluminescence from catalytically grown CdSe nanobelts and sheets", R. Venugopal, P.-I. Lin, C.-C. Liu, and Y.-T. Chen; *Journal of American Chemical Society*, submitted (2005).

We have successfully fabricated single-crystalline CdSe nanowires, nanobelts, and sheets by a chemical vapor deposition (CVD) method assisted with laser ablation. The synthesized CdSe nanostructures have hexagonal wurtzite phase as characterized by X-ray diffraction (XRD). CdSe nanobelts can range in length from several tens to a hundred of μm, thickness from 40 to 70 nm, and a tapered width which is ~3 μm at one end and tapers off to ~100 nm at a catalytic gold particle. Both selected area electron diffraction (SAED) and high-resolution transmission electron microscopic (HRTEM) measurements show that the single-crystalline hexagonal belts and sheets grew along the [0 1 -1 0] direction with side surface of ±(0 0 0 1) and top surface of ±(2 -1 -1 0). While the growth mechanism of nanobelts complies with a combination of VLS and vapor-solid (VS) processes, the formation of sheets is primarily based on VS mechanism. For comparison, the phonon modes of CdSe nanobelts and bulk powder have been measured by SERS and normal Raman scattering (NRS) spectroscopies with off- and near-resonant excitations. A blue-shift of 2.4 cm^{-1} for the longitudinal optical (LO) phonon of CdSe nanobelts, relative to bulk CdSe, is attributed to a lattice contraction in the belt structure, which is confirmed by the XRD measurement. Room-temperature micro-photoluminescence (PL) at ~1.74 eV from single CdSe nanobelts shows a threefold enhancement comparing with that from bulk CdSe powder, and displays a partial polarization dependence of emission angles.