93　5　31

NSC91-2113-M-002-035

91 　　 8 　　 1 　　　 92 　　　 10 　　　 31

(　　　　　　　　　　　)

93 　　　 5 　　　 28

.

REMPI　　　　　　　　　　-h₅ (CH₂CHCH₂)　　　*n*s (*n* = 4-12) Rydberg

-d₅ (CD₂CDCD₂)　　*n*s (*n* = 4-10) Rydberg　　　(6.0–8.2 eV)

*n*s Rydberg　　　　　　　　　　　　　　　8.133 ± 0.001 eV　　　　-d₅

(CD₂CDCD₂)　　　　　　8.124 ± 0.002 eV　　　　　1+1　2+2 REMPI　　　　　2-

(CH₂C(CH₃)CH₂)　$\tilde{B}\,(1^2A_1) \leftarrow \tilde{X}\,(1^2A_2)$　$\tilde{C}\,(1^2B_2) \leftarrow \tilde{X}\,(1^2A_2)$　$\tilde{E}\,(2^2A_2) \leftarrow \tilde{X}\,(1^2A_2)$

38000–41000 cm⁻¹　　　　　　　　　　　　1+1 REMPI　　41000–43500 cm⁻¹

~80 cm⁻¹　　　　$\tilde{D}\,(2^2B_2) \leftarrow \tilde{X}\,(1^2A_2)$　$\tilde{F}\,(3^2B_2) \leftarrow \tilde{X}\,(1^2A_2)$

$\tilde{C}\,(1^2B_2) \leftarrow \tilde{X}\,(1^2A_2)$

-　　　　Rydberg

193 nm　ArF　　　　　　　　　SiO₂　　　　　　　7 nm　　15 nm

1.9 eV　　　　　　　　　　Si-O•　　　　2.35 eV　　　　Si-H

2.75 eV

2.35 eV　2.75 eV

MCM-41　　　　　　　　　1.905, 1.78, 1.61, 1.40, 1.27 and 1.14 eV　　　　Si-O•

1.905 eV　　　　　　Si-O• 1.78 eV　　　　　Si-O•　　1.61, 1.40, 1.27

1.14 eV　　Si-O•　　　　　　　1.905 eV　1.78 eV

(SBA-15)-AgI　-　　　　　　　　　　　　　　AgI　　　　SBA-15

AgI　　　SBA-15

AgI　SBA-15　　　　　　　　　　　　2.38 eV　Si-H　　　　　　AgI

AgI　　　　SiO₂　　　　Si-H

2.38 eV

M²⁺/kaolin (M = Fe, Co, Ni, Cu)　　　　　　400−2000 nm

90%　　　　　　600−800 nm　　　　　　0.33−0.35 nm

KMnO₄　H⁺　　　　　　　　　　HF　48%

SiO₂　Fe, Ru,　Pr　　　　　　　　　　　　　　　　≥ 5 nm

~ μm)　　　　　　　　Si {111}

vapor-liquid-solid　　　　　　　　FeSi₂　RuSi₃

PrSi₄　　　　　　　<111>　　　SiO₂

<112>

:　　　　2-　　　　　　　　　　　　MCM-41　　SBA-15

· **Abstract**

The vibronic spectra of allyl-h_5 (CH_2CHCH_2) and allyl-d_5 (CD_2CDCD_2) radicals at 6.0-8.2 eV and 2-methylallyl radical ($CH_2C(CH_3)CH_2$) at 4.6–5.6 eV have been observed using resonance-enhanced multiphoton ionization (REMPI) spectroscopy. Rydberg states of ns (n = 4-12) for allyl-h_5 and (n = 4-10) for allyl-d_5 have been identified. The adiabatic ionization energies, 65594 ± 9 cm^{-1} (8.133 ± 0.001 eV) for allyl-h_5 and 65527 ± 16 cm^{-1} (8.124 ± 0.002 eV) for allyl-d_5, are extrapolated from the convergence of the observed ns Rydberg series. In another REMPI spectroscopic study, $\tilde{B}(1^2A_1) \leftarrow \tilde{X}(1^2A_2)$, $\tilde{C}(1^2B_2) \leftarrow \tilde{X}(1^2A_2)$ and $\tilde{E}(2^2A_2) \leftarrow \tilde{X}(1^2A_2)$ of 2-methylallyl radical at 38000–41000 cm^{-1} are identified. Much broader 1+1 REMPI signals at 41000–43500 cm^{-1} with HWHM of ~80 cm^{-1} for each vibronic band could be due to $\tilde{D}(2^2B_2) \leftarrow \tilde{X}(1^2A_2)$ and/or $\tilde{F}(3^2B_2) \leftarrow \tilde{X}(1^2A_2)$ via an intensity borrowing from $\tilde{C}(1^2B_2) \leftarrow \tilde{X}(1^2A_2)$.

Photoluminescence (PL) from composites of 7- and 15-nm silica (amorphous SiO_2) nanoparticles and bulk type-III fused silica induced by two-photon band-to-band excitation with 193-nm (6.4-eV) ArF laser light has been measured in time-resolved detection mode. The PL spectra taken for 15-nm particles allow us to identify three PL bands peaked in the red (~1.9 eV), green (~2.35 eV), and blue (~2.85 eV) spectral ranges, which are assigned to nonbridging oxygen hole centers, hydrogen-related species, and self-trapped excitons (STE's), respectively. As a result of time-resolved measurements, the extremely broad PL band peaked at ~2.35 eV, which is typically observed for bulk silica and initially assigned to STE's, is found to consist of two bands peaked at ~2.75 and ~2.35 eV. We conclude that these bands are due to the radiative deexcitation of STE's and hydrogen-related centers, respectively. The STEPL band is peaked at ~2.75 eV for both bulk amorphous and crystalline SiO_2.

Experimental study of room temperature PL from silica nanoparticles and mesoporous silica at 1.905, 1.78, 1.61, 1.40, 1.27 and 1.14 eV have been assigned due to the bulk non-bridging oxygen (NBO) defects at 1.905 eV, surface NBO at 1.78 eV, and oxygen vacancy (OV) in various positions to the NBO defects at 1.61−1.14 eV. We have shown that combined defects including NBO and an oxygen vacancy (OV) in various positions exhibit the suitable properties (both energies and oscillator strengths) to be responsible for the observed PL bands. These combined defects are proposed to occur in extremely thin (~1 nm) non-equilibrium substoichiometric silicon oxide (SiO_x, x<2) layers. The emphasis is on the PL band shift induced by one, two and three OV's in the nearest vicinity of NBO, and the influence of the Si-Si bond relaxation in OV's as well as the orientation of NBO's and distances between them and OV's on transition energies and oscillator strengths. PL from mesoporous silica is evidenced to originate from non-bridging oxygens (NBO's) located inside ~1-nm pore walls and on the pore internal surfaces. Based on *ab initio* calculations, we showed that the PL band diversity in the range of 1.0–2.1 eV results from both isolated bulk and surface NBO's and those combined with variously placed pore wall oxygen vacancies.

Synthesized (SBA-15)-AgI host-guest nanocomposites were characterized by powder X-ray diffraction analysis, indicating that AgI has been prepared in the channels of SBA-15 molecular sieve host. As the guest loading decreases, a blue-shift was observed in the solid diffuse reflectance absorption spectra. This shows that the guest existed in the channels of SBA-15 and a quantum confinement effect emerged. The PL spectra show that the PL at ~2.38 eV, associated with the hydrogen-related species, decreases substantially after the loading of AgI in SBA-15. The decrease of the PL indicates the reduction of the hydrogen concentration on the pore surface of SBA-15 after the loading of AgI guest.

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 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.

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.

Keywords: allyl radicals, 2-methylallyl radicals, SiO_2 nanoparticles, MCM-41, SBA-15 mesoporous materials, photoluminescence, Si nanowires.

. Report

In the past academic year, we have focused on the studies of (1) resonance-enhanced multiphoton ionization spectroscopy of excited polyatomic valence and Rydberg states, and (2) preparation and optical characterization of nanoscale materials. The research publications are summarized as follows.

A. Summary of publications

1. Resonance-enhanced multiphoton ionization spectroscopy

Vinyl chloride (C_2H_3Cl)	"*Ab initio* calculations of low-lying electronic states of vinyl chloride" *Journal of Chemical Physics*, <u>116</u>, 7518-7525 (2002).
Allyl radical (C_3H_5)	"Two-photon resonant ionization spectroscopy of the allyl-h_5 and allyl-d_5 radicals: Rydberg states and ionization energies" *Journal of Chemical Physics*, <u>116</u>, 4162-4169 (2002).
2-Methylallyl radical (C_4H_7)	"One- and two-photon excitation vibronic spectra of 2-methylallyl radical at 4.6-5.6 eV" *Journal of Chemical Physics*, <u>119</u>, 241-250 (2003).
REMPI reviews	"Applications and advances of resonance-enhanced multiphoton ionization spectroscopy" *Trends in Chemical Physics,* <u>4</u>, pp. 21-46 (Research Trends, India, 2002).
	"Molecular Rydberg states and ionization energy studied by two-photon resonant ionization spectroscopy" *Journal of Chinese Chemical Society*, <u>49</u>, 703-722 (2002).

2. Preparation and optical characterization of nanoscale materials

a. Photoluminescence spectroscopy

SiO_2 nanoparticles	"Time-resolved photoluminescence study of silica nanoparticles as compared to bulk type-III fused silica" *Physical Review B,* <u>66</u>, 035404 (2002).
MCM-41	"Red and near-infrared photoluminescence from silica-based nanoscale materials: Experimental investigation and quantum chemical modeling" *Journal of Chemical Physics,* <u>116</u>, 281-294 (2002).
	"Photoluminescence from mesoporous silica akin to that from nanoscale silicon: The nature of light-emitters" *Chemical Physics Letters,* <u>358</u>, 180-186 (2002).

b. Synthesis and optical properties

SBA-15 "Optical properties of host(SBA-15)-guest(AgI) composite materials"
Journal of Chinese Chemical Society, <u>50</u>, 59-64 (2003).

Carbon nanospheres "Synthesis and properties of carbon nanospheres grown by CVD using Kaolin supported transition metal catalysts"
Carbon, <u>42</u>, 813-822 (2004).

c. One-dimensional nanowires

Silicon nanowires "Catalytic growth of silicon nanowires assisted by laser ablation"
Journal of Physical Chemistry B, <u>108</u>, 846-852 (2004).

B. Description of the accomplishments

1. Resonance-enhanced multiphoton ionization spectroscopy (References are listed in A.1.)

Two spin-forbidden transitions, $\tilde{b}(1\,^3A'') \leftarrow \tilde{X}(1\,^1A')$ and $\tilde{c}(2\,^3A'') \leftarrow \tilde{X}(1\,^1A')$, of vinyl chloride are calculated to locate in 5.5-6.5 eV, and could be responsible for the observed one-photon absorption spectrum due to an intensity borrowing caused by the spin-orbit coupling of the Cl atom. Based on calculation, we conclude that upon the excitation of vinyl chloride at 193 nm, the $\tilde{b}(1\,^3A'')$ or $\tilde{c}(2\,^3A'')$ excited state, instead of the (π, π^*), is initially prepared prior to the subsequent photodissociation processes.

The vibronic spectra of allyl-h_5 (CH_2CHCH_2) and allyl-d_5 (CD_2CDCD_2) radicals at 6.0-8.2 eV have been observed using 2+1 resonance-enhanced multiphoton ionization (REMPI) spectroscopy. Rydberg states of ns (n = 4-12) for allyl-h_5 and (n = 4-10) for allyl-d_5 have been observed in the REMPI spectra. Prominent vibrational progressions with the spacings of ~440 cm^{-1} in allyl-h_5 and ~360 cm^{-1} in allyl-d_5 are observed in the s Rydberg series. The totally symmetric $\angle$CCC-bending mode is responsible for the vibrational progressions. Facilitated with *ab initio* calculated Franck-Condon factors, other vibrations (CH$_2$ rocking and C$_3$ stretching) observed in the s Rydberg series have also been identified. The adiabatic ionization energies, 65594 ± 9 cm^{-1} (8.133 ± 0.001 eV) for allyl-h_5 and 65527 ± 16 cm^{-1} (8.124 ± 0.002 eV) for allyl-d_5, are extrapolated from the convergence of the observed ns Rydberg series.

Vibronically excited 2-methylallyl radical ($CH_2C(CH_3)CH_2$) at 4.6–5.6 eV has been studied by 1+1 and 2+2 REMPI spectroscopy. The 2-methylallyl radicals were produced by the flash pyrolysis of 3-bromo-2-methylpropene in a supersonic-jet expansion. The 2+2 REMPI spectrum

of 2-methylallyl radical at 38000–40700 cm^{-1} is identified as the $\tilde{B}(1^2A_1) \leftarrow \tilde{X}(1^2A_2)$ transition, i.e. the excitation of a non-bonding electron to the 3s Rydberg state ($3s \leftarrow n$). Seven lowest-lying electronic states with excitation energy below 6 eV have been calculated in an MRCI level. Two new electronic bands have been observed at 38500–41000 cm^{-1} by 1+1 REMPI spectroscopy and assigned to $\tilde{C}(1^2B_2) \leftarrow \tilde{X}(1^2A_2)$ and $\tilde{E}(2^2A_2) \leftarrow \tilde{X}(1^2A_2)$. Much broader 1+1 REMPI signals at 41000–43500 cm^{-1} with HWHM of ~80 cm^{-1} for each vibronic band could be due to $\tilde{D}(2^2B_2) \leftarrow \tilde{X}(1^2A_2)$ and/or $\tilde{F}(3^2B_2) \leftarrow \tilde{X}(1^2A_2)$ via an intensity borrowing from $\tilde{C}(1^2B_2) \leftarrow \tilde{X}(1^2A_2)$. Taking the computed geometries and vibrations of the ground and excited electronic states, Franck-Condon factors have been calculated. Combining the FCFs with the calculated excitation energies and oscillator strengths of the six electronic states at 4−6 eV, predicted spectral patterns have been used to assist spectroscopic analysis for the observed vibronic spectra of 2-methylallyl radical.

2. Preparation and optical characterization of nanoscale materials

a. Photoluminescence spectroscopy
   ### (References are listed in A.2.a.)

Photoluminescence (PL) from composites of 7- and 15-nm silica (amorphous SiO$_2$) nanoparticles and bulk type-III fused silica induced by two-photon band-to-band excitation with 193-nm (6.4-eV) ArF laser light has been measured in time-resolved detection mode. The PL spectra taken for 15-nm particles allow us to identify three PL bands peaked in the red (~1.9 eV), green (~2.35 eV), and blue (~2.85 eV) spectral ranges. The green and blue bands are normally overlapped in conventional scan measurements, giving no way for determining their exact peak positions. Similar red and green PL bands were observed for 7-nm particles, whereas the blue band extends toward the higher-energy range and is peaked at ~3.25 eV. The aforementioned red, green, and blue PL bands are assigned to nonbridging oxygen hole centers, hydrogen-related species, and self-trapped excitons (STE's), respectively. The red and green PL bands for bulk type-III fused silica are peaked at practically the same spectral positions as those for nanoscale silica, indicating the similarity of light-emitter types. However, the blue band for bulk silica used is peaked at ~2.75 eV, that is, at typical position for STE's in crystalline SiO$_2$. The blueshift of STE (PL) (STEPL) band with decreasing nanoparticle size is consistent with the previously proposed model of phonon-assisted radiative relaxation of STE's. As a result of time-resolved measurements, the extremely broad PL band peaked at ~2.35 eV, which is typically observed for bulk silica and initially assigned to STE's, is found to consist of two bands peaked at ~2.75 and ~2.35 eV. We suggest that these bands are due to the radiative deexcitation of STE's and hydrogen-related centers, respectively. We thus conclude that the STEPL band is peaked at ~2.75 eV for both bulk amorphous and crystalline SiO$_2$.

Experimental study of room temperature PL from silica nanoparticles and mesoporous silica

induced by ultraviolet and visible laser light (λ_{exc} = 266 and 532 nm or 4.66 and 2.33 eV, respectively) reveals several well-defined PL bands in the red and near-infrared spectral range, which are peaked at 1.905, 1.78, 1.61, 1.40, 1.27 and 1.14 eV. The relative intensities of the bands depend on the specimen heat pretreatment temperature and excitation wavelength. The band at 1.905 eV shows all conceivable characteristics of non-bridging oxygen (NBO) defects in bulk silica, so it can be assigned to the same species in nanometer-sized SiO_2 fragments. The more slowly decayed 1.78-eV band was assigned to NBO's incorporated into distorted SiO_4 tetrahedrons on the surface. The 1.14-1.61 eV PL bands can be observed mainly with 2.33-eV excitation for heat pretreated specimens (T_{ht} = 873 and 1173 K) and can also be associated with NBO's. The red shift of these bands is explained in terms of formation of combined defects involving NBO as an electron acceptor and an additional point defect in NBO vicinity serving as a donor, with the electronic energy level somewhat higher than the bottom of the forbidden band gap. Using sophisticated quantum chemical modeling [geometry optimization of model clusters containing up to 60 Si and O atoms employing 2-layered integrated molecular orbital ONIOM method [I. Komaromi *et. al.*, J. Mol. Struct. (Theochem) **461**, 1 (1999)] followed by time-dependent density functional calculations of excitation and PL energies] we have shown that combined defects including NBO and an oxygen vacancy (OV) in various positions exhibit the suitable properties (both energies and oscillator strengths) to be responsible for the observed PL bands. These combined defects are proposed to occur in extremely thin (~1 nm) non-equilibrium substoichiometric silicon oxide (SiO_x, x<2) layers. The emphasis is on the PL band shift induced by one, two and three OV's in the nearest vicinity of NBO, and the influence of the Si-Si bond relaxation in OV's as well as the orientation of NBO's and distances between them and OV's on transition energies and oscillator strengths. The results of calculations closely match the PL peaks observed. Since silicon nanoscale materials are typically covered by non-equilibrium substoichiometric passivating oxide layers as well, our findings may also be helpful to clarify the nature of light emission from these materials.

PL from mesoporous silica is evidenced to originate from non-bridging oxygens (NBO's) located inside ~1-nm pore walls and on the pore internal surfaces. Based on *ab initio* calculations, we showed that the PL band diversity in the range of 1.0–2.1 eV results from both isolated bulk and surface NBO's and those combined with variously placed pore wall oxygen vacancies. The spectroscopic features are found to be similar to those of surface-oxidized silicon nanocrystals and porous silicon. The results obtained are expected to be useful to clarify the nature of light-emitters in silicon nanoscale materials.

b. Synthesis and optical properties
(References are listed in A.2.b.)

Nanoclusters AgI has been prepared in the channels of SBA-15 molecular sieve host, and the host-guest nanocomposite materials were prepared by a heat diffusion method. The (SBA-15)-AgI host-guest nanocomposites were characterized by powder X-ray diffraction

analysis, nitrogen adsorption-desorption isotherms at 77 K, and solid-state diffuse reflectance absorption spectra. The decrease in surface area, pore diameter, and pore volume showed the existence of silver iodide clusters in the channels of SBA-15 host. X-ray diffraction illustrates that the framework of the SBA-15 remained in the host-guest composites of (SBA-15)-AgI. As the guest loading decreases, a blue-shift was observed in the solid diffuse reflectance absorption spectra. This shows that the guest existed in the channels of SBA-15 and a quantum confinement effect emerged. The PL spectra show that the PL at ~2.38 eV, associated with the hydrogen-related species, decreases substantially after the loading of AgI in SBA-15. The decrease of the PL indicates the reduction of the hydrogen concentration on the pore surface of SBA-15 after the loading of AgI guest. The intensity decrease of the self-trapped exciton (STE) band at 2.76 eV also suggests a hindrance for generating the excitons upon adding the AgI guest into the SBA-15 host.

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.

c. Synthesis and optical properties
   ## (References are listed in A.2.c.)

Silicon nanowires (SiNWs, dia. ≥ 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 have been discussed. Pressure effect on the longitudinal and transverse growing rates in the fabrication of SiNWs has been examined.