

行政院國家科學委員會專題研究計畫 期中進度報告

應用於太陽能轉換之新穎氮化銦/二氧化鈦奈米結構薄膜之 製備及其電子移轉研究(1/3)

計畫類別：個別型計畫

計畫編號：NSC94-2120-M-009-014-

執行期間：94 年 08 月 01 日至 95 年 07 月 31 日

執行單位：國立交通大學應用化學系(所)

計畫主持人：李遠鵬

共同主持人：林恭如，李積琛，刁維光

計畫參與人員：李遠鵬，刁維光，李積琛，林恭如，鍾昭宇，駱立揚，鄭棋文

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 95 年 6 月 6 日

奈米國家型科技計畫 學術研究重要成果表

填表日期：95 年 5 月 16 日

1. 計畫背景：(請以中、英文並呈)

計畫主持人及共同主持人 (PI and Co-PIs)：

PI: 李遠鵬 (Yuan-Pern Lee)

Co-PIs: 刁維光 (Eric Wei-Guang Diau)、李積琛 (Chi-Shen Lee)、
林恭如 (Gong-Ru Lin)

研究題目 (Project Title)：

應用於太陽能轉換之新穎氮化銦/二氧化鈦奈米結構薄膜之製備及其電
子移轉研究

Preparation and Interfacial Electron Transfer of Novel InN/TiO₂
Nanocrystalline Thin Films for Solar Energy Conversion Applications

主持人執行機構 (Organization、Institution)：

國立交通大學應用化學系 (Department of Applied Chemistry, NCTU)

國立交通大學光電工程學系 (Institute of Electro-Optical Engineering, NCTU)

全程計畫執行期限 (Project Period)：

自民國 94 年 08 月 01 日起至民國 97 年 07 月 31 日

2. Goals of the project (Don't exceed 300 words)

We propose to investigate collaboratively the preparation and characterization of novel InN/TiO₂ nanoparticle-film and relevant systems for solar energy conversion. An important goal of this project is to set up an advanced ultrafast laser laboratory to use various cutting-edge spectral techniques to investigate electron/energy transfer dynamics of various nanomaterials; it will be beneficial to many researchers in nanoscience in Taiwan. We will focus on the fabrication and characterization of InN/TiO₂ nanocrystalline films with different materials embedded at the interface of the InN and TiO₂ films to modify the system's optical band gap and to promote electron transfer rates from InN to TiO₂ and back-transfer to the sensitizer for enhancement of solar energy conversion efficiencies. The materials to be embedded and protected by the InN film include nanoparticles and/or thin films of semiconductors and conductors. In addition, mixed nanoparticle films of TiO₂ and other metal oxides with lower band gaps such as WO₃ and SnO₂ will also be employed in lieu of pure TiO₂ for band gap modification and potential improvement in solar energy conversion efficiencies. Characterization of all fabricated films will be carried out by surface and film morphology analyses, interfacial electron transfer dynamics, and direct photo-current measurements of these solar cell devices. The key interfacial electron transfer dynamics between InN and TiO₂ will be extensively investigated with various time-resolved spectroscopy techniques in both UV/VIS and IR regions, including femtosecond fluorescence up-conversion, transient UV/VIS absorption/reflectance, ultrafast IR spectroscopy, and step-scan time-resolved FTIR. The intermediate excited states and the electrons in the semiconductor will be directly probed with these techniques to provide information on the mechanism and the temporal evolution of interfacial electron transfer.

4. Please list all the participants of the project, including names and affiliations.

	Name	Affiliation
PI	Yuan-Pern Lee	Dept. Applied Chemistry, NCTU
Co-PI	Eric Wei-Guang Diau	Dept. Applied Chemistry, NCTU
Co-PI	Chi-Shen Lee	Dept. Applied Chemistry, NCTU
Co-PI	Gong-Ru Lin	Inst. Electro-Optical Engineering, NCTU
Co-PI	Niann-Shia Wang	Dept. Applied Chemistry, NCTU
As-PI	Ming-Chang Lin	Dept. Applied Chemistry, NCTU
Postdoctor	Chia-Yan Wu	Dept. Applied Chemistry, NCTU
Research Assistant	Su-Ching Chuang	Dept. Applied Chemistry, NCTU
Research Assistant	Kuo-Hua Huang	Dept. Applied Chemistry, NCTU
Ph.D. student	Yu-Chung Wu	Department of Chemistry, NTHU
Ph.D. student	Chao-Yu Chung	Department of Chemistry, NTHU
Ph.D. student	Liyang Luo	Dept. Applied Chemistry, NCTU
Master's student	Chi-Wen Cheng	Dept. Applied Chemistry, NCTU
Undergraduate	Cheng-Yao Tsai	Dept. Applied Chemistry, NCTU

5. Please list at most six most important publications after your project has started for six months.

1. "Femtosecond Fluorescence Dynamics of Porphyrin in Solution and Solid Films: The Effects of Aggregation and Interfacial Electron Transfer between Porphyrin and TiO_2 ", L.-Y. Luo, C.-F. Lo, C.-Y. Lin,* I-J. Chang, and E. W.-G. Diau*, J. Phys. Chem. B **110**, 410 (2006).
2. "Evidence for the Assembly of Carboxyphenylethynyl Zinc Porphyrins on Nanocrystalline TiO_2 Surfaces", C.-F. Lo, L.-Y Luo, E. W.-G. Diau,* I-J. Chang, and C.-Y. Lin*, ChemComm 1430 (2006).
3. "Formation of Nanostructures of Hexaphenylsilole with Enhanced Color-Tunable Emissions", C. J. Bhongale, C.-W. Chang, E. W.-G. Diau*, C.-S. Hsu, Y. Dong, and B.-Z. Tang, Chem. Phys. Lett. **419**, 444 (2006).
4. "Relaxation Dynamics and Structural Characterization on Formation of Organic Nanoparticles with Enhanced Emission", C. J. Bhongale, C.-W. Chang, C.-S. Lee, E. W.-G. Diau*, and C.-S. Hsu, J. Phys. Chem. B **109**, 13472 (2005).
5. "Relaxation Dynamics of 2,7- and 3,6-Distyrylcarbazoles in Solutions and in Solid Films: Mechanism for Efficient Non-radiative Deactivation in the 3,6-linked Carbazole", T.-T. Wang, S.-M. Chung, F.-I. Wu, C.-F. Shu, and E. W.-G. Diau*, J. Phys. Chem. B **109**, 23827 (2005).
6. "Time-resolved photoluminescence analysis of multidosed Si-ion-implanted SiO_2 ", C.-J. Lin, C.-K. Lee, and G.-R. Lin,* J. Electrochem. Soc. **153**, E25 (2006).
Selected by Virtual Journal of Ultrafast Science, Vol. 5, No. 1, January 2006.

6. Please describe outstanding results achieved in your project with relevant figures, tables and comparison with other similar works in the world. (Don't exceed 1,000 words)

At the initial stage, three parts (preparation, dynamics, and characterization) are developed in parallel. They will be integrated at the end of this project.

A. Preparation of nano materials

(1) Metal oxide nanocrystals

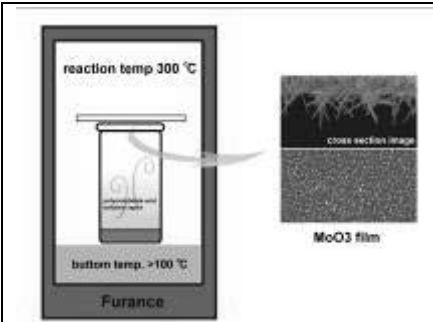
- (a) MoO₃ nanomaterials (Figure 1): A novel method for growing quasi aligned MoO₃ nanorod film on glass substrate using water soluble precursor via the vapor-pyrolysis-deposition process is developed (Scheme 1). SEM, TEM selected-area electron diffraction and powder X-ray analyses indicate that the MoO₃ rods are growing along [010].
- (b) WO₃ nanocube and VO_x nanowires (Figures 2, 3): The deposition process for MoO₃ nanorod film has been extended to other metal oxide systems to produce WO₃ nanocube and VO_x nanowire. The former might be a potential material to replace anatase TiO₂ in solar cell and the study for the energy conversion efficient is in progress. This synthetic route to deposit VO_x rods or wires on glass substrate is new.
- (c) ZnO nanomaterials (Figures 4–6): A novel two dimensional coordination polymer Zn(tda)H₂O (tda = O(CH₂COO)₂²⁻) was synthesized under hydrothermal condition. The structure features two dimensional, noncentrosymmetric networks with a pseudo hexagonal network of Zn(II) coordinated by tda and water molecules. Thermodecomposition behavior of Zn(tda)H₂O using synchrotron powder diffraction (Figure 4) indicates that the structure in Zn(tda)H₂O remains intact when H₂O is removed. The Zn(tda)H₂O decomposed at T > 550 C to form ZnO/ZnS sponge with a surface area ~ 30 m²/g. The SEM images show extensive connection of thick flakes with an average thickness of 100 nm and a fine structure of a single flake showing countless thin crystalline sheets with average thickness of 10 nm. The method requires only one solid precursor and may be used to prepare ZnO thin film for photovoltaic studies.

(2) Sonochemical method for metal chalcogenide nanoparticles

The goal of this study was to prepare stable visible-light absorbing semiconductor nanoparticles for use as an inorganic sensitizer on photovoltaic solar cell. Figure 7 shows preliminary results of In₂Se₃, In₂Te₃, Sb₂Te₃ and Bi₂Te₃. The products of metal chalcogenides exhibit irregular particle and rod forms depending on the compound.

(3) Deposition of InN on TiO₂

The growth of nanocrystalline InN on TiO₂ is achieved by a homemade plasma enhanced chemical vapor deposition (PE-CVD) system (Fig. 8). The trimethyl indium (TMIn) and NH₃ are precursors. Figure 9 shows the photocurrent of InN/TiO₂ as a function of wavelength. The photocurrent depends on the size of TiO₂, deposition temperature, and annealing; the maximal photocurrent is about 2μA at 380 nm.



Scheme 1

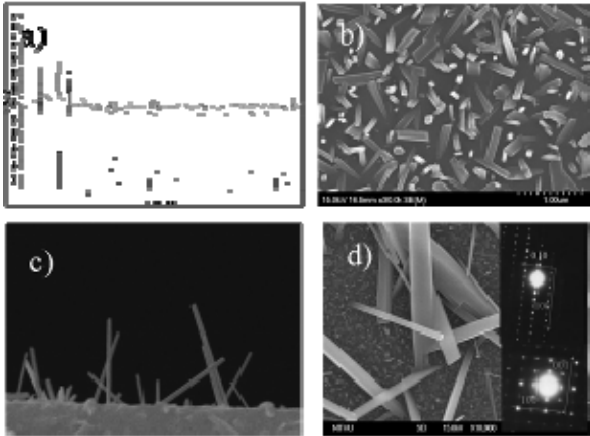


Figure 1. (a) XRD pattern of MoO₃ bulk (red) and nanorod film (pink). (b) SEM image for top view of the quasi-aligned MoO₃ nanorods film. (c) SEM image of MoO₃ rods observed from the edge of glass substrate. (d) SEM image of an enlarged MoO₃ nanorod. Inset: SAED patterns showing <001> and <010> zone axes.

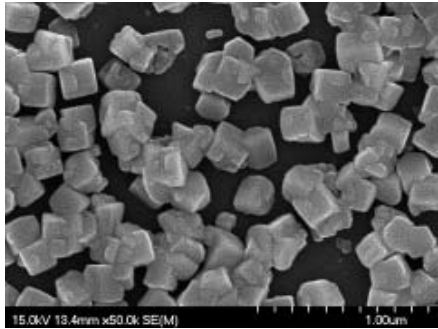


Figure 2. The SEM image of WO₃ nanocube deposited on a glass substrate.

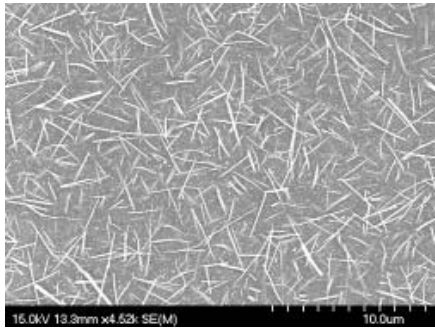


Figure 3. The SEM image of VO_x nanowires.

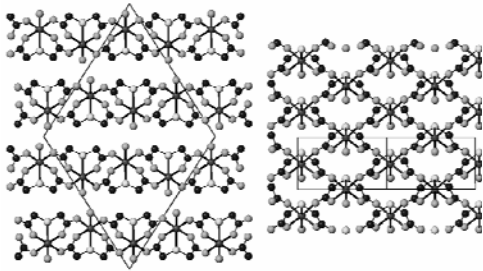


Figure 4. a) The three dimensional structure Zn(tda)H₂O projected along [010]. b) 2D structure of Zn(tda)H₂O.

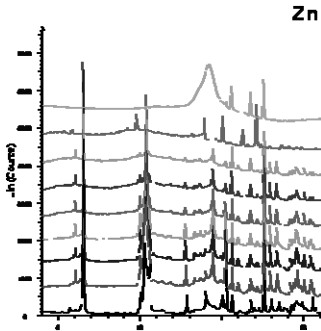


Figure 5. Temperature-dependent synchrotron powder diffraction patterns for Zn(tda)H₂O recorded at 25, 245, 250, 255, 260, 265, 270, 300, 500 °C, and complete dehydrate reaction occurs to porous ZnO (from bottom to top)..

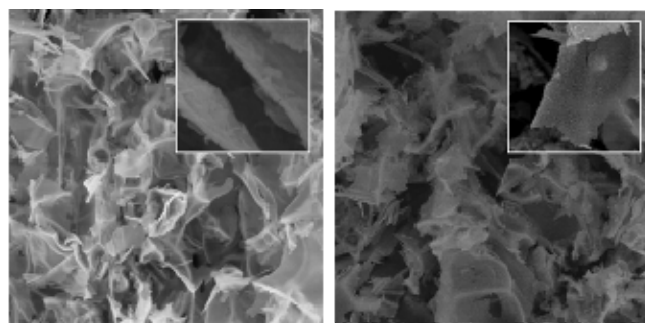
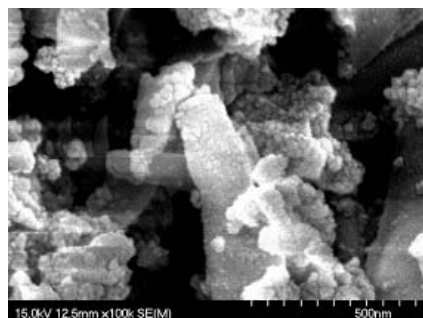
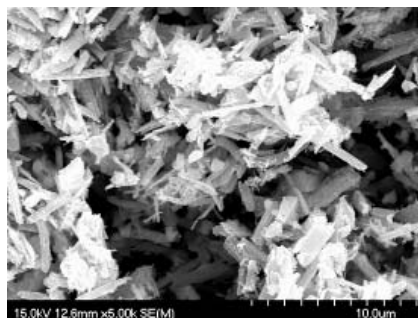


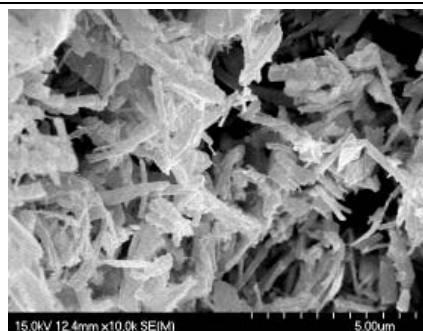
Figure 6. SEM images porous ZnO + ZnS (left) and porous ZnO (right). Insets are magnified pictures showing fine structure of flakes.



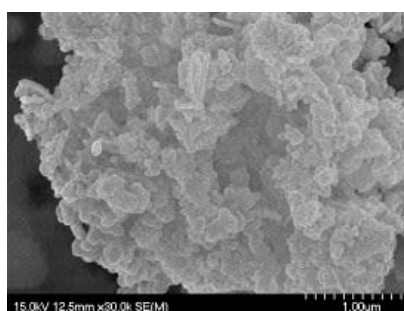
a) In_2Se_3



b) In_2Te_3



c) Sb_2Te_3



d) Bi_2Te_3

Figure 7. SEM images of a) In_2Se_3 , b) In_2Te_3 , c) Sb_2Te_3 , d) Bi_2Te_3

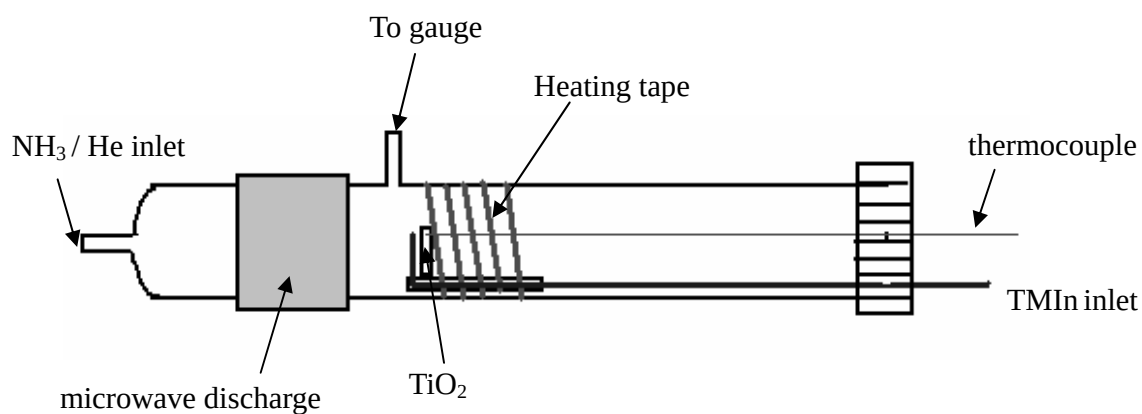


Figure 8. Schematic diagram of the homemade plasma enhanced chemical vapor deposition (PE-CVD) system.

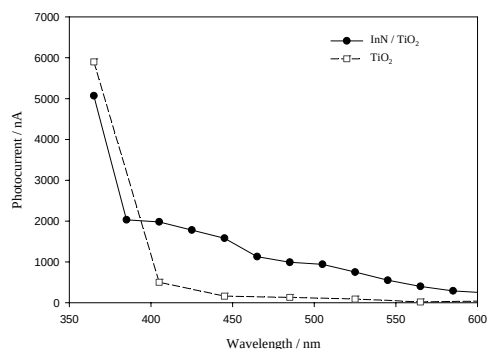


Figure 9. Photocurrent—irradiation wavelength measurement for a InN/TiO₂ cell.

B. Dynamics studies using ultrafast lasers

(1) Femtosecond fluorescence up-conversion measurements

The interfacial electron transfer process (IET) of the porphyrin/TiO₂ system is investigated using fluorescence up-conversion technique for the first time. The fluorescence decay opens a narrow window in the early stage and thus provides crucial information on the nature of the excited state of the sensitizer before the electron injection occurs. Results for observed ultrafast IET process between the porphyrins (ZnCAPEBPP and ZnCATPP) and the TiO₂ nanocrystalline film are given in Figure 10.

The IET process occurs on TiO₂ film but was absent on glass film. Photocurrents of these systems are shown in Figure 11. The IET transfer rate of ZnCAPEBPP/TiO₂ film is faster than that of ZnCATPP/TiO₂ film, consistent with an improved incident photon to current efficiency (IPCE) for the former. A much better π -conjugation for ZnCAPEBPP than for ZnCATPP is responsible for the higher IET efficiency observed for the former.

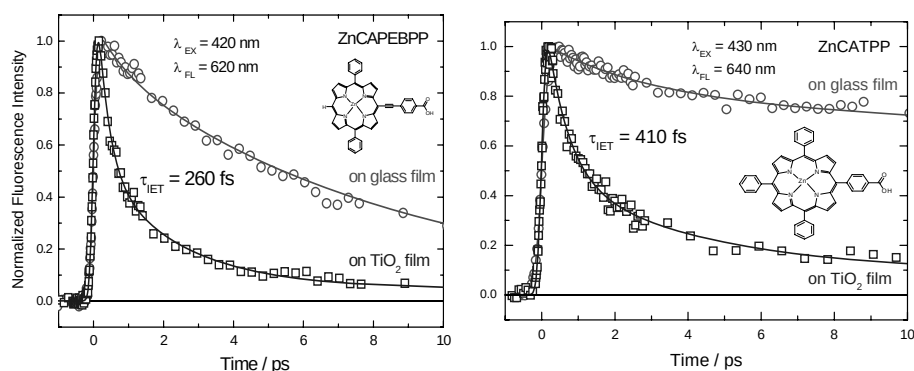


Figure 10. Femtosecond fluorescence decays of two different porphyrins on glass and TiO₂ nanocrystalline thin films.

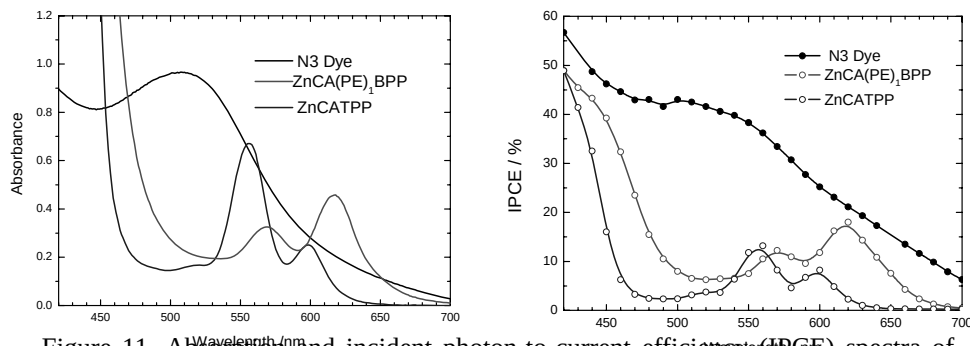


Figure 11. Absorption and incident photon-to-current efficiency (IPCE) spectra of two porphyrins on TiO₂ films. The N3 dye/TiO₂ thin-film sample was also shown.

(2) Femtosecond transient absorption measurements

A femtosecond transient absorption spectroscopy system has been set up. The source includes a regenerating amplifier system; wavelength of the laser pulse is selected with two optical parametric amplifiers (OPAs), as shown in Figure 12. The pump-probe spectrometer uses the output of the OPA as a pump pulse to excite the molecule into its excited state and subsequent relaxation dynamics were probed by a white light pulse generated by a delayed laser pulse, as shown in Figure 13.

We have carried out transient absorption measurements for the ZnCAPEBPP/TiO₂ thin-film sample with S₂ excitation ($\lambda_{\text{ex}} = 435$ nm). Observed decays (Figure 14) show two additional features as compared with previous results (τ_1 and τ_2) obtained from fluorescence method; the prominent offset component reflects the detection of the cation species, and the “slow” decay component (τ_3) is probably associated with the electron-hole recombination process.

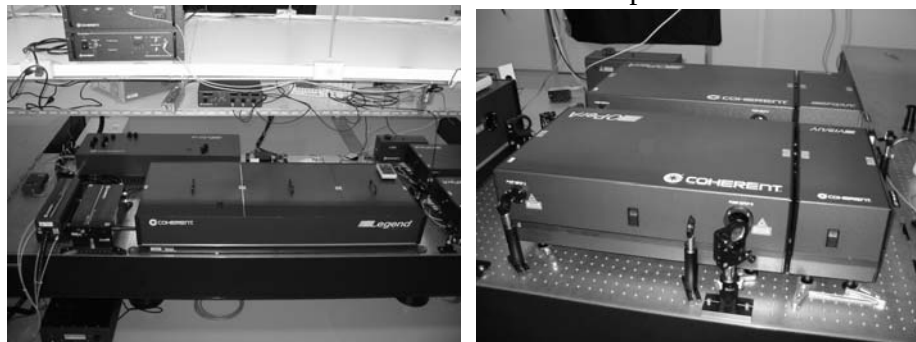


Figure 12. Experimental setup of our femtosecond laser system which includes a regenerating amplifier (left) and two OPAs (right).

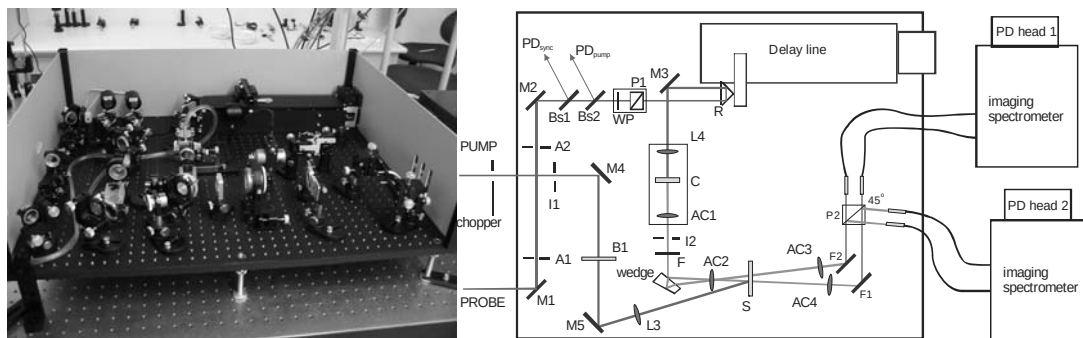


Figure 13. Equipmental setup of femtosecond transient absorption spectrometer (left) and its optical layout (right).

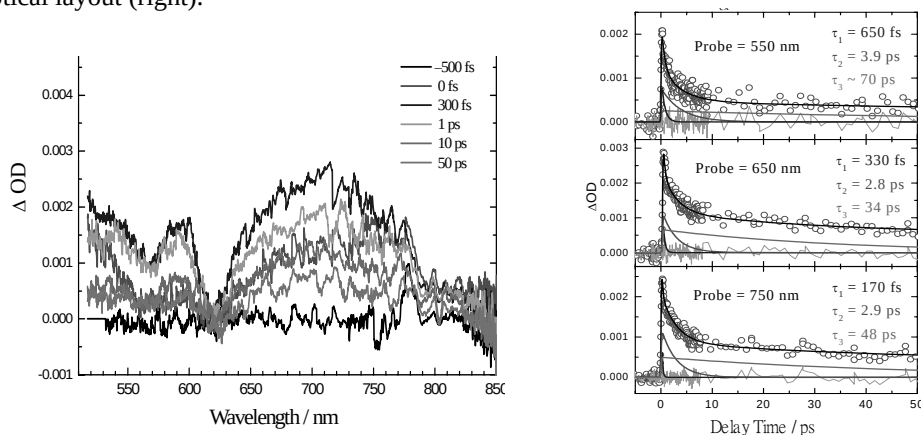


Figure 14. Femtosecond transient absorption spectra (left) and three corresponding relaxation dynamics (right) of the ZnCAPEBPP/TiO₂ films with excitation at 435 nm.

C. Fabrication and characterization of solar cell

A Green laser based testing system has been assembled for characterizing the photocurrent-voltage response of solar cell devices. Electrical and optoelectronic diagnostics of the solar cell can be performed using this probe station. Feature functions of the probe station are:

1. Photocurrent-voltage response using monochromatic light,
2. Modulation photocurrent response,
3. Conversion efficiency analysis.

This system includes a micro-probe station with lightwave coupling fiber bundle and a 150 mW diode-pumped YAG laser at wavelength of 532 nm. Coupling with an I-V-R source meter, the photovoltaic effect of the InN/TiO₂ solar cell is characterized, as shown in Fig. 15. With this station, the photocurrent and optical responsivity of the synthesized materials for fabricating solar cell devices can be evaluated.

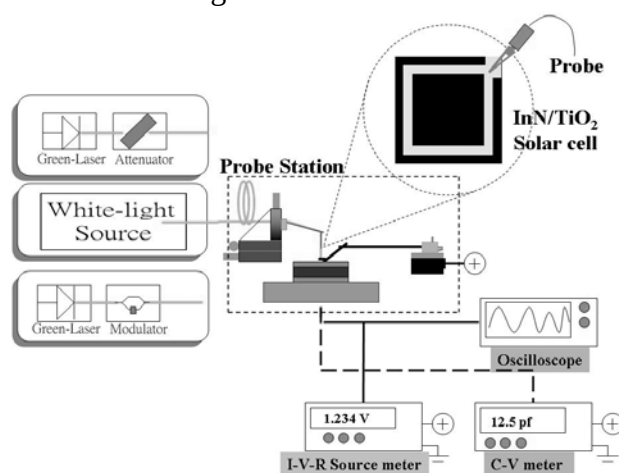


Figure. 15. Setup of diagnostic center for characterizing InN/TiO₂ solar cell

6. Please list at most five international conferences you were invited to give oral and plenary talks. Please also list international prizes you won in last three years.

1. Gong-Ru Lin, "White-light and near-infrared electroluminescence of furnace or CO₂ laser annealed Si-rich SiO₂ with structural defects and Si nanocrystals", **2006 SPIE Symposium on Photonics Europe (PE 2006)**, paper 6195-32, Strasbourg, France, April 3-6, 2006.
2. Gong-Ru Lin, "Retrospect on the Research of Silicon Nanocrystal Embedded Silicon Oxide Materials and Light-Emitting Devices in NCTU/IEO", **3rd Symposium on Nanophotonics Science and Technology**, Hualian, Taiwan, September 13-17, 2005