行政院原子能委員會
委託研究計畫研究報告

【應用於太陽能轉換之量子點敏化 InN/TiO₂ 奈米粒子薄膜研發】
【Quantum-Dot Enhanced InN/TiO₂ Nanoparticle Films for Solar Energy Conversion Applications】

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中文摘要

本計畫是為期四年行政院原子能委員會委託研究計畫之第三年執行結果摘要。本年的主要工作在進行以下目標：(一)利用plasma-enhanced及organometallic chemical vapor deposition (PECVD及OMCVD)的方法完成第一階段製作InN/TiO₂量子點太陽電池,結果與去年NREL之Nozik認為有相當高效率的InAs/TiO₂量子點太陽電池效率近似；(二)完成InN/-OB(O)O/TiO₂及InN/OP(O)O/TiO₂系統之連鍵(-OY(O)O-, Y=B及P)效率的比較,前者有明顯的效率增加,而後者明顯的降低,此結果顯示化性強壯的HOB(O)O化學鍵可利用為其他半導體量子點接連TiO₂奈米薄膜的主要工具(諸如CdSe, Si, Ge, ZnO等)。

此外,一系列的半導體量子點(QD)及奈米粒子(NP)亦用水熱法製作,諸如ZnO, M-doped ZnO (M=Fe, Co), In₂O₃及InTe。此類QD及NP將可利用為InN/QD(NP)/TiO₂的介面導電物質。

未來一年將在新的In(M)N/Linker/d-TiO₂奈米光電系統逐步改進三構件(components)：(1)敏化量子點InN加入不同的dopants (M=Ga, Al, Zn, Sb…)；(2)化學聯結鍵(Linker), -OY(O)O<(Y=B, P, Al, Si, Zn…)的變化應用；及(3) TiO₂奈米基板加入dopants (d=B, P, Zn, W…)。有系統的調製三構件,配合飛秒雷射作電子轉移動態的測量,期以導致一件高效率、化性物性堅牢的太陽電池,供給水分解的應用。
Abstract

This is the report for the third year of the 4-year proposal on the III-V metal nitride nanoparticle-enhanced TiO₂ solar cell, initially focussing on the InN/TiO₂ nanoparticle system.

In the proposed studies at NCTU, our emphasis has been placed primarily on the development of an economically viable solar energy conversion system for photovoltaic and, most importantly, for photo-electrochemical water-splitting applications. The low-cost, nontoxic and chemically and thermally stable properties of TiO₂ have resulted in much recent research effort to circumvent its large band gap (3.2 eV or 387 nm) by modifying its surface optical properties for applications in the visible region of the spectrum, specifically for solar energy conversion. The best known technique to enhance its photovoltaic efficiency is Graetzel’s method using dyes to improve its photo-absorption cross section and electron transfer dynamics.

The best dye employed by Graetzel and co-workers, RuL(SCN)₃, has reached ~10% solar energy conversion efficiency under their best operational conditions. It is comparable to amorphous silicon systems with 9-10% efficiencies and is less than that of polycrystalline silicon devices which have been reported to reach >15% efficiency. It should be noted that both the organic dye/TiO₂ and polycrystalline Si systems are costly and still cannot compete economically with fossil fuels such as coals and natural gases.

In the past year, we have completed the first phase of InN/TiO₂ employing two different InN deposition techniques, PECVD (Plasma enhanced chemical vapor deposition) and OMCVD (organometallic
CVD) using the TiO$_2$ nanoparticle films prepared by the common sol gel method. The fabricated InN/TiO$_2$ devices by both methods have now reached the best device fabricated by Nozik et al. of NREL published last year.

In another series of experiments, we have achieved a critical milestone by carefully analyzing the effects of B(OH)$_3$ vs P(OH)$_3$ as linkers between InN and TiO$_2$. The results indicate clearly that the $-\text{OB(O)O}$-anchoring group enhances the InN/TiO$_2$ photocurrent, whereas the $-\text{OP(O)P}$-group pronouncedly reduces the photocurrent. The theoretical underpinning of this critical finding is currently under quantum-chemical study on their binding characteristics.

In addition to these important milestones, we have continued the syntheses of a variety of semiconductor quantum dots for future incorporation into the interface between InN and TiO$_2$, for example, InTeX, ZnO and M-ZnO (M=Fe, Co, etc.). Once the cavities of the top layer TiO$_2$ nanoparticle films can be effectively increased and enlarged, these QDs will be employed for the fabrication of InN/QD/TiO$_2$ devices.
壹、計畫緣起與目的

由於天然能源的缺乏，台灣每年約有 98 %的能源仰賴進口。因此，台灣應該優先地投資在再生能源的研究領域。在此科學領域中，台灣已遠遠落後於日本、美國和歐洲。太陽是一個取之不盡、用之不竭的天然資源，因此有效率地使用太陽能應是二十一世紀最重要的科技挑戰之一。

此計畫將在交通大學執行，但和核能所密切合作。我們主要著重於發展一個具經濟效益的太陽能轉換系統以應用在太陽能光電轉換及/或光電化學上分解水的研究。二氧化鈦(TiO₂)的低成本、無毒性、及化學及熱穩定的性質，使得相當多的研究群組致力於研究如何透過表面光學特性的修飾以克服其較大的 band gap (3.2 eV 或 387 nm)，以將其應用於可見光區，尤其是太陽能之轉換。而提升其光電效率的最著名的技術乃是 Graetzel’s 所發展出以染料改進半導體之光吸收截面積及電子轉移動態學的方法。

Graetzel 等人使用最理想的染料，在最佳的實驗條件下，已可達到 10 %的太陽能轉換效益，其轉換效益和非晶形矽系統的 9-10 % 相當，但比多晶形矽系統的>15 %差。值得注意的是，有機染料/TiO₂及多晶形矽系統之成本尚高，其經濟效益仍然無法與石化燃料，如與石碳及天然氣相比。

於是我們希望可以利用半導體量子點取代有機染料，改善其不穩定的缺點。在半導體量子點敏化的研究中，選用矽、氮化銦及其他半導體或導體作為吸收太陽能的敏化物。矽及氮化銦量子點的能隙依其粒子大小而定，大約是 1.6 ev 左右，可以吸收太陽光中大
量的辐射能量(太阳光中已可见光及红外光含量最多)。

在Emory大学，林明璋研究组已经成功地利用低压有机金属化学蒸发法（OMCVD），使用HN₃及In(CH₃)₃，将所产生的InN薄膜沉积在已被吸附固定于sapphire片或Ti金属上的TiO₂奈米粒子上¹。此沉积的InN/TiO₂奈米粒子薄膜呈现非常宽广的390-800nm紫外/可见光吸收谱带，其吸收光区与Graetzel²等人的black dye/TiO₂系统所量測的结果相当类似。此半导体的InN/TiO₂薄膜其稳定的化学性或著有助其利用於光电转率及水分解应用上的耐用性。在后者的应用上，已有类似但昂贵的方法使用InGaP/GaAs光电极可达到令人印象深刻的各种效率³。相较於InGaP/GaAs系统在光电化学之应用上，InN/TiO₂奈米粒子薄膜其化学性能更稳定且制造成本更便宜。

InN/TiO₂奈米薄膜在光电转换之电子转移等物理特性将利用交通大学的超快雷射技术来研究，而其光电能产生及转移的效率则可以利用光电流的直接量测而得到。在台湾，超快雷射技术应用於凝態的研究，交通大学应用化学系居於领先之地位。

除了我们所量測到增强的InN/TiO₂薄膜在紫外/可见光区吸收，最近Nozik等人已经偵测到以InP及InAs量子点吸附在TiO₂奈米薄膜上，其在紫外/可见光区之吸收有显著的提升⁴,⁵。由于物理吸附之作用力通常是不强，且InP及InAs不夠耐用，所以Nozik的InX/TiO₂(X=P, As)系统大概无法维持长久的使用，尤其在溶液中使用。因此，是否可以利用有机金属蒸发法以一层化性稳定之InN薄膜，将这些量子点包覆起来？若能够这样做，这些以InN包覆的InX量子点或其他类别的高效率光电转换材料所产生的光电子是否能有效
率地轉移到 TiO₂上？這些是我們在發展一個有效率和具經濟效益的光電轉換及水分解系統的過程中，希望能有系統來探討的問題。

在此計畫中，我們擬議研究以 InN 奈米粒子或薄膜覆蓋其他半導體奈米粒子的效應。最初，我們將研究嵌入 Si, InP 及其他半導體兩種量子點在 InN 和 TiO₂奈米薄膜之間，如前所述。Si 和 InP 均具有相似之能隙(分別為 1.1 與 1.3 eV)。除此之外，我們將以其他金屬氧化物之量子點或奈米粒子修飾 TiO₂基版，以改變 TiO₂的能帶邊 (band edge)，使其與 InN 奈米薄膜或量子點的重疊變為最大。除此以外，InN 及 TiO₂之間的接連化鍵及 TiO₂奈米薄膜的 dopant 效應 (諸如 n-或 p- dopant 影響光電效應)的研究，亦為未來本計劃的研發重點。

References:
貳、研究方法與過程

一、Preparation of semiconductor nanoparticles（C. S. Lee）:

Synthesis of Metal Chalcogenide and Metal Oxide Nanoparticles

The goals of this project are to prepare and characterize new semiconductor and metal oxide nanoparticles to fabricate thin film electrode for solar cell applications. This report covers the time period of January 1 - December 31, 2007. Several nanomaterials have been synthesized and tested include: 1) Au incorporated In(OH)$_3$ and In$_2$O$_3$: A new synthetic route to grow In(OH)$_3$ and In$_2$O$_3$ nanocrystals of rectangular shape and incorporating Au is presented. The elemental Au is deposited on the surface of In(OH)$_3$ rectangular nanocrystals as a thin film and incorporated into In$_2$O$_3$ nanoporous material as nanoparticles. 2) Morphology controlled Co$_x$Zn$_{1-x}$O: A systematic approach to synthesize Co$^{2+}$ doped ZnO nanocrystals with controlled particle shape has been developed. The Co$^{2+}$ doped ZnO exhibit strong absorption in visible light region, which could affect the photo energy conversion of metal oxide film made up of Co-ZnO nanoparticles. 3) InTe nanoparticles on TiO$_2$ film: the influence of the InTe quantum dot on photovoltaic performance was observed with best efficiency of 0.134% under illumination by simulated AM 1.5 solar light (100 mW/cm$^2$). During this year six conference posters were presented. 1-6

Materials with confined structures have attracted much research, especially metal oxides incorporating metal nanoparticles that are potentially useful for applications including catalysts, photocatalysts, solar cells etc. Among such reported materials, ZnO,
In(OH)$_3$ and In$_2$O$_3$ are of particular interest due to their peculiar physical properties. They are both wide band-gap semiconductors. A thin film of In(OH)$_3$ exhibits conductivity in a range $10^{-7}$–$10^{-3}$ S/cm$^2$ and In$_2$O$_3$ nanomaterials show satisfactory electrical conductivity and a high sensitivity towards some gases. ZnO is a wide band-gap semiconductor which doping with transition metal impurities has been widely investigated as a strategy for extending the photo responses into the visible spectral range, thereby making them suitable candidates for photochemical conversion of solar energy into electrical or chemical potential. For low band gap semiconducting materials, it has been considered as the alternative source of sensitizer for solar cell device. Our studies have been focused on the preparation of semiconductor nanomaterials in varies binary systems and TiO$_2$ anatase nanoparticle films. As these metal-incorporating oxide materials are prospectively applicable for solar cell, our research has focused on discovering new synthetic routes to deposit a metal element or semiconductor nanoparticles on metal-oxide nanoparticles to assemble thin film electrode for solar cell. In this report, we report the synthesis and optic property studies of Au-doped In(OH)$_3$/In$_2$O$_3$ nanoparticles, Co:ZnO nanoparticle with controlled shape, and InTe/TiO$_2$ film.

Experimental

1. Synthesis

(1) Synthesis of In(OH)$_3$ and In$_2$O$_3$: In a typical experiment, sodium hydroxide solution (10 M, 72 mL) was added dropwise to InCl$_3$ solution (0.3 g, 1.35 mmol) under vigorous stirring at 23 °C. The milky-white colloid suspension was subjected to
vigorously stirring and sonic treatment for at least 30 min before being transferred to a Teflon-lined stainless-steel autoclave (capacity 23 mL) and heated at 160 °C for 20 h. The white precipitate of In(OH)₃ was washed thoroughly with DI water under ultrasonic condition (240 W output), centrifuged and finally dried in vacuum to collect the product. Nanoporous In₂O₃ shows a light yellow color, obtained on calcination of In(OH)₃ in a crucible at a temperature 450 °C and maintained in air for 2 h.

(2) Synthesis of Au-incorporating In(OH)₃ and In₂O₃: A sodium hydroxide solution (72 mL, 10 M) was added dropwise to InCl₃ (0.3 g, 1.35 mmol) under vigorous stirring at 23 °C, followed by slow addition of HAuCl₄ solution (5 %) until the molar ratio Au/In = 1. The light yellow solution was subjected to vigorous stirring and sonic treatment for at least 30 min before being transferred to a Teflon-lined stainless-steel autoclave (capacity 23 mL) and heated at 160 °C for 20 h. The violet-red precipitate was washed thoroughly with DI water under ultrasonic conditions (240 W output), then centrifuged and finally dried in vacuum to collect the product of Au-In(OH)₃. The powder as prepared was calcined in a crucible at a temperature 450 °C and maintained for 2 h in air to form Au-incorporating In₂O₃ with a similar violet-red color.

(3) Synthesis of ZnO nanorods on ITO film: A thin film of zinc oxide was coated on the ITO substrate by doctor blade method (thickness ~ 5 um) with a solution containing nanoparticles of zinc oxides. ZnO nanoparticles were prepared by
(6) Synthesis of InTe Nanoparticles: InTe nanoparticles were prepared by mixing a solution of InCl$_3$, Te element in solution of trioctylphosphine (TOP). The mixed solution was heated for 2 – 60 min at 180 °C under nitrogen atmosphere. Formation of the InTe nanoparticles is accompanied by the appearance of an intense dark brown color. The as synthesized nanoparticles were diluted with toluene and precipitated with methanol. The precipitate was dissolved in pyridine and precipitated again in an excess amount of methanol. The resulting black suspensions were centrifuged and the precipitates were washed three times with absolute methanol. The as synthesized nanoparticles were diluted with toluene and precipitated with methanol. The precipitate was dissolved in pyridine and precipitated again in excess amount of methanol.

2. Characterization

XRD, UV, PL, SEM, TEM, TGA, BET: The product as prepared was characterized by XRD (Bruker AXS D8 Advance, Leipzig Germany, Cu K$_\alpha$ radiation at 40 kV and 40 mA), SEM (Hitachi, S-4700I, operated at 15kV), TEM (JEOL, JEM-3000F, operated at 200 kV), UV-vis absorption spectra (Hitachi, U-3010 spectrometer, scanning wavelength 190 nm~1000 nm, Al$_2$O$_3$ plate as reference), thermogravimetric analysis (TGA, Perkin-Elmer Pyris, T = 50 - 750°C, rate 10 °C/min), and PL measurements (Jobin-Yvon Spex Fluorolog-3, $\lambda_{ex} = 365$ nm, filter wavelength = 400 nm, Xe lamp, 23 °C, scanning wavelength 400 - 800 nm). Surface areas were determined by the BET method from the adsorption of nitrogen at 77 K with a
surface area analyzer (NOVA 1000e-Series). The unit-cell parameters were obtained on refining the maxima of the XRD patterns with a least-squares refinement method using the CELREF program (Langmuir, J.; Bochu, B. Celref; http://www.inpg.fr/LMGP; Laboratoire des Materiaux et du Ge’nie Physique de l’Ecole Supe’rieure de Physique de Grenoble.). Current-voltage (I-V) measurements were performed using a solar simulator with output intensity AM1.5 (100 mW/cm²).

3. Results

(1) Au- incorporated In(OH)₃ and In₂O₃ nanoparticles: With InCl₃ and HAuCl₄ as precursors under basic conditions, In(OH)₃ and In₂O₃ nanomaterials incorporating elemental gold were synthesized by a hydrothermal process and thermal decomposition. Both Au-incorporating products appear violet-red (Figure 1a). XRD patterns of Au-incorporating In(OH)₃ and In₂O₃ samples match the diffraction features of not only In(OH)₃ and In₂O₃ but also metallic Au (Figure 1b). The SEM image of the Au-In(OH)₃ sample shows nanocrystals of rectangular shape with edge length 20~60 nm. After complete decomposition at 450 °C, the In(OH)₃ nanocrystals of rectangular shape were fully transformed into In₂O₃ with no significant alteration of the overall morphology (Figure 2). Transmission electron microscopy (TEM) for a In(OH)₃ single crystal exhibits rectangular shape and selected-area electron diffractions (SAED) exhibit [001] zone-axis diffraction of bcc In(OH)₃ (inset of Figure 3a), indicative of a single-crystalline
Figure 3b shows a TEM image from an Au-incorporating In(OH)$_3$ single crystal that is covered with a thin film of unknown material (thickness ~ 1 nm). The SAED pattern clearly shows a four-fold axis that can be indexed with hk0 of In(OH)$_3$, indicative of a single-crystalline In(OH)$_3$ nanocrystal. EDS measurements show the existence of Au, In and O elements. These results indicate that the In(OH)$_3$ nanocrystal is covered with a thin layer of elemental gold. An area scan of elemental Au on the surface of In(OH)$_3$ nanocrystals shows an uneven distribution of Au, indicating that the surface of the In(OH)$_3$ nanocrystal is incompletely covered by Au. Figure 3c is a TEM image of an In$_2$O$_3$ nanobundle of rectangular shape that exhibits a highly porous morphology formed by interconnected indium-oxide nanocrystals with average pore diameter 3-5 nm. The wall thickness is about 5 nm for most aggregated rectangular bundles. Selected-area electron diffraction (SAED) performed on an In$_2$O$_3$ bundle revealed a pattern of rings and dots that is indexed to cubic In$_2$O$_3$, indicative of the polycrystalline nature of the nanoporous In$_2$O$_3$ product. When Au is incorporated into this In$_2$O$_3$ nanoporous material, the shape of the Au-In$_2$O$_3$ bundle is essentially the same as the In$_2$O$_3$ product with small pores of diameter ~ 3 nm; this form is unprecedented for an indium-oxide nanostructure (Figure 3d). An EDS area scan for elemental Au show a scattered distribution of Au signal, indicating that the Au element was incorporated into the In$_2$O$_3$ rectangular bundle. The results indicate that the Au film in
In(OH)$_3$ melted during calcination to form small particles of Au, which diffused further into the nanoporous In$_2$O$_3$ bundle. The BET surface areas of Au-In(OH)$_3$ and Au-In$_2$O$_3$ are 26.2 and 35.5 m$^2$/g, respectively, comparable with a commercial nanoparticle sample of In$_2$O$_3$ for which the surface area is 27 m$^2$/g. The results are consistent with a porous structure according to the SEM/TEM measurements.

The UV diffuse reflection spectra of both Au-incorporating samples show clearly an intense absorption maximum about 532 nm, attributed to the surface-plasma excitation of gold nanoparticles (Figure 4a). The band gaps of In(OH)$_3$ and In$_2$O$_3$ host materials are calculated to be 5.57 and 3.74 eV, respectively, which are similar to reported values. Photoluminescence (PL) spectra of both In$_2$O$_3$ and Au-In$_2$O$_3$ nanoporous materials show a strong and broad PL emission in the blue-green region with its maximum intensity centered at 467 nm; this sharp blue-green emission is attributed to the radiative recombination of a photo-excited hole with an electron occupying oxygen vacancies in the In$_2$O$_3$ host, analogous to the PL mechanism of ZnO defect nanocrystals. During the thermal decomposition, oxygen vacancies are expected to be generated at a large concentration because of O and H bonds released and In$_2$O$_3$ crystallization. Similar PL spectra with maxima in the blue-green region are reported for In$_2$O$_3$ nanoparticles, nanocubes and nanofibers.

According to the experimental observations we propose a mechanism for the formation of the Au-incorporating
nanomaterials. As illustrated in Figure 4b, the \( \text{Au(OH)}_4^- \) complexes were initially attached at the surface of \( \text{In(OH)}_3 \) colloids during the hydrothermal process. The \( \text{Au}^{3+} \) ions became subsequently reduced by chloride ion under basic conditions according to this reaction:

\[
2 \text{Au(OH)}_4^- + 3\text{Cl}^- + 2\text{OH}^- \rightarrow 2\text{Au} + 3\text{ClO}^- + 3\text{H}_2\text{O}
\]

The reduced elemental \( \text{Au} \) covers the surface of \( \text{In(OH)}_3 \) nanocrystals. During thermal decomposition, the newly formed indium oxide begins to form on the surface of \( \text{In(OH)}_3 \). The O and H bonds of molecules were released within the \( \text{In(OH)}_3 \) nanocrystal and caused the formation of small voids or pores until indium hydroxide is completely decomposed to form nanoporous indium oxide. The \( \text{Au} \) film melted to form \( \text{Au} \) nanoparticles, which diffused into the pores or interstitial regions of \( \text{In}_2\text{O}_3 \) bundles.

(2) Synthesis \( \text{ZnO} \) nanorod film and \( \text{Co}^{2+} \) doped \( \text{ZnO} \) nanoparticles and nanorod: SEM image of \( \text{ZnO} \) nanorods on ITO film reveals average diameter and length of \( \text{ZnO} \) nanorod of \( \sim 50 \) and 100 nm, respectively (Figure 5a). The as-synthesized \( \text{ZnO} \) rod/ITO films were used as the metal oxide electrode to fabricate solar cell device. The photocurrent measurements of ITO film covered by \( \text{ZnO} \) nanorods reveals photo energy conversion efficient of 0.04 %, which is higher than the ITO film with \( \text{ZnO} \) nanoparticles (\( \eta = 0.018 \) %). The results indicate that the \( \text{ZnO} \) nanorod could enhance the solar cell activity. The study for the effect of size in \( \text{ZnO} \) rods to photo currents is in progress. The \( \text{Co}^{2+} \) doped \( \text{ZnO} \)
nanoparticles were synthesized with different wt% of Co$^{2+}$ and the SEM images for Co-ZnO nanoparticles are shown in Figure 6a. The results indicate that the initial amount of Co$^{2+}$ ion affect the shape of Co-ZnO nanocrystals that varied from needle shape (10, 20, 40 wt%) to rod shape (80 %) and finally to hexagonal rod shape crystals (120, 200%). UV-vis spectra shows band gap absorption at $\lambda \sim 400$ nm and ligand field absorption in the visible light region between 550 and 700 nm (Figure 6b). The intensity of ligand field absorption is increase as the Co$^{2+}$ doping concentration is raised.

(3) The effect of InTe nanoparticles to photocurrent: The InTe nanoparticles were synthesized under different condition to study their effect to photocurrent (Table 1). Solar cell devices with films of InTe/TiO$_2$ were fabricated for photocurrent measurements (Figure 7). When small amount of InTe nanoparticles was introduced to the film, the photocurrent increased. The film with crystalline InTe nanoparticles exhibits the most pronounce photo energy conversion efficiency.

4. Conclusion

In(OH)$_3$ and In$_2$O$_3$ nanocrystals of rectangular shape and incorporating Au film and nanoparticles have been successfully prepared using a hydrothermal reaction followed by thermal decomposition. This procedure will be readily generalized to prepare other metal-incorporating nanoporous metal-oxide materials to serve as catalyst, gas sensor, and quantum-dot solar cell substrate. The Co$^{2+}$ doped ZnO nanoparticles show strong absorption in visible light region and their particle shape and
thermodecomposition of Zn(tda)H$_2$O. The as-prepared ZnO coated ITO substrate was placed to a solution of zinc nitrate (5 mM, 98%, Riedel-de Haën) and hexamethylenetetramine (HMTA; 99%, Alfa-Aesar), follow by heating at T = 95 °C for 2 h.

(4) Synthesis of Co$^{2+}$ doped ZnO nanoparticles: A solution of zinc nitrate (5 mM, 98%, Aldrich) and hexamethylenetetramine (HMTA; 99%, Aldrich) was prepared to mix with different amount of Co(NO$_3$)$_2$6H$_2$O (97.7%, Alfa-Aesar). The weight percentage of Co(NO$_3$)$_2$6H$_2$O was varied to 10, 20, 40, 80, 120, and 200 % compare to zinc nitrate. The reactions were carried out at T = 95 °C for 2 h.

(5) Synthesis of TiO$_2$ nanocrystals: Nanocrystalline TiO$_2$ in anatase form was synthesized via a combined sol–gel process with hydrothermal treatment. In typical synthesis, a specified amount of 2-propanol (10 ml) was first introduced into Ti(OR)$_4$ (37ml). The mixed solution was then gently added drop wise into a solution of water (250 ml) and acetic acid (80 ml) under N$_2$ flow. The solution became pale blue solution after the process was done. The mixture was continuously stirred at 80 °C for 3 hours to obtain white sol. Then, the gel was cooled to room temperature to become pale blue, transparent solution. Subsequently, the gel was dried at 80 °C 3 hrs, the dried sample was calcined at 500 – 700 °C for 1 – 24 h to produce the desired mesoporous TiO$_2$ photocatalyst. The spin coating method was used to prepare TiO$_2$ film.
Co$^{2+}$ concentration is tunable. The deposition of crystalline InTe nanoparticles to TiO$_2$ film show enhancement of photocurrent.

Figure 1. a) Appearance of Au-In(OH)$_3$ and Au-In$_2$O$_3$ powder samples, b) Powder x-ray diffraction patterns of Au-In(OH)$_3$ and Au-In$_2$O$_3$.

Figure 2. SEM images of In(OH)$_3$ and In$_2$O$_3$ and their corresponding Au-incorporated nanocrystals.
Figure 3. TEM images and corresponding SAED patterns (insets) of (a) In(OH)$_3$, (b) Au-In(OH)$_3$, (c) In$_2$O$_3$ and (d) Au-In$_2$O$_3$.

Figure 4. a) UV-vis diffuse reflectance spectra of Au-In(OH)$_3$ (black) and Au-In$_2$O$_3$ (red). b) A schematic illustration for the transformation of an Au-incorporating indium hydroxide rectangular nanocrystal to a nanoporous indium oxide rectangular nanobundle through hydrothermal and thermal decomposition.

Figure 5. a) SEM image of an ITO film covered by ZnO nanorod. b) I–V curves of solar cells based on films of ZnO nanoparticle/ITO film (red) and ZnO nanorod/ITO film (black). The I$_2$/I$^-$ solution was used as electrolytes; light intensity was 100 mWcm$^{-2}$ from an AM 1.5 source).
Figure 6. a) UV diffuse reflectance spectra for products of Co$^{2+}$ doped ZnO nanoparticles. The labeled percentages of Co$^{2+}$ are based on the experiment amount of Co(NO$_3$)$_2$·6H$_2$O weight percentage. b) SEM images of Co$^{2+}$ doped ZnO nanoparticle with different staring weight percentage of Co$^{2+}$.

Table 1. Summary of reaction conditions for InTe synthesis.

<table>
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<th>Rxn</th>
<th>Rxn. Conditions</th>
<th>Temp</th>
<th>Quench</th>
<th>η</th>
<th>V</th>
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<td>0.114(0) 0.490(0) 0.48(2) 0.48(1)</td>
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</table>

Figure 7. a) I–V curves of solar cell devices based on films of InTe nanoparticle/TiO$_2$ film with InTe nanoparticles from reaction InTe01-InTe07. b) Powder x-ray pattern of InTe sample from InTe07 reaction. b) SEM image of InTe/TiO$_2$ film.
References:


3. M.-C. Wu and C.-S. Lee, “Synthesis and Characterization of Heterometallic Coordination Polymers M'_{x}M''_{1-x}(tda)H_{2}O (M' and M'' =Zn, Co and Ni, 0<x<1)” in The 8th Conference of the Asian Crystallographic Association, Taipei, Taiwan, 2007.


二、Characterization of semiconductor nanoparticles (K. W. Sun):

1. Research methods and processes

   (1) Visible light absorption and Photoluminescence from Co doped ZnO nanorods: The co-doped ZnO nanorods with different Co compositions are prepared by Prof. C.S. Lee’s research group. The nanorod under investigation has an average length of 1 µm and a diameter of 200~300 nm. The Co dopants can introduce impurity levels in the ZnO bandgap to enhance absorption of the ZnO in the visible light wavelength range. The micro-PL from the impurity levels are studied by excited the ZnO (Co)$_x$ with a DPSS laser operated at wavelength of 488 nm. The emission is recorded through a confocal microscope equipped with a 0.32m spectrometer and a liquid-nitrogen cooled CCD.
(2) Nano PN junction for Si solar cell: Through E-Beam lithography and epi-layer growth techniques, we have fabricated PN diodes with nano meter scale junctions. The I-V characteristics of the diodes with nano junction are measured with a probe station. The reduced junction cross-section can reduced the dark current (thermal generation current in the diode depletion regions) by an order of magnitude. The reduction of dark current can lead to the increase of Si solar cell conversion efficiency and detectivity of Si photodiode.

(3) Charge transport in the TiO₂ film: We have devised a time-of-flight measurement system to investigate the photocurrent transient in TiO₂ solar cells. We compare the results between TiO₂ solar cells prepared with different solvents. The faster decay of photocurrent indeed reflects on the better conversion efficiency of the solar cell.

2. Main discoveries and conclusions

(1) Visible light absorption and Photoluminescence from Co doped ZnO nanorods: A broad absorption peak from 550 nm to 680 nm is observed in the absorption spectrum of the ZnO(Co)ₓ, as shown in Figure 1. Figure 2 to 4 show the emission peaks at visible wavelengths from 566 nm to 684 nm. The emission peaks are resulted from the doped Co impurity levels in the mid-gap of ZnO.
(2) Nano PN junction for Si solar cell: An Oxide layer of thickness of 100 nm is first grown on a 4 inch Si wafer after the RCA cleaning processes. The nanostructured templates were prepared using electron-beam (e-beam) lithography techniques on Si (001) substrates. The flow chart of the lithography and etching processes is given in Figure 5. Nanopore patterns were directly written in a square area of about 200 µm x 200 µm with an electron - beam writer operated at a fixed electron voltage of ~ 50 KV. By using the patterned ZEP-520 as the hard mask, the exposed Si area was then etched into the substrate with a depth of approximately 120 nm below the Si surface via the chemical wet etching processes. In Figure 6 we show the SEM images of the nanopores on one the templates we made.
A layer of p-type amorphous silicon is grown on the nanostructured template by via PECVD to form the nano PN junction. The TEM image of the junction cross section is shown in Figure 7. The results of the I-V measurement of the device is shown in Figure 8.
(3) Charge transport in the TiO$_2$ film: Two TiO$_2$ solar cells made from P25 powder are prepared with the solvents of HNO$_3$ and Acetic acid. The I-V characteristics of the two solar cells are shown in Figure 9. The solar cell prepared with the HNO$_3$ solvent gives a better performance on the conversion efficiency over the cells prepared with the Acetic acid. In Figure 10, the time-of-flight measurements also show shorter photocurrent decay time for the cells using HNO$_3$ solvent. It indicates that it is much easier for the electrons to transport in the TiO$_2$ film prepared with HNO$_3$ solvent.

References:


InN/TiO₂ solar cells by PECVD and OMCVD:

1. InN/TiO₂ nanoparticles by PECVD (C. W. Lu, Y. P. Lee and M. C. Lin)

TiO₂ nanoparticles were prepared according to a method similar to that reported by Zaban and coworkers.¹ The sol-gel solution with a TiO₂ nanoparticle colloid was synthesized via a controlled hydrolysis of titanium (IV) isopropoxide, Ti(–OC₃H₇)₄ (Aldrich, 97 %) in an aqueous solution of glacial acetic acid at 273 K. The solution was then heated to 353 K for 8 h before being autoclaved at 503 K for 12 h. The resulting TiO₂ sol-gel solution was spread onto a clean Ti foil or a conducting glass substrate (FTO, F-doped SnO₂, sheet resistance 10 Ω cm⁻²) and baked in an oven at 723 K for 1 h to form TiO₂ films with nanoparticles of typical sizes 20–30 nm. TiO₂ nanoparticles of big sizes could be prepared on increasing the autoclaved temperature.

Figure 1 is a schematic diagram of the experiment for PECVD. The reactor is a quartz tube (diameter 5 cm) with a sidearm (diameter 0.6 cm, length 5 cm) for pressure measurements; the reactor is evacuated with an oil mechanical pump. A controller (Omega, CN9000) regulated the reaction temperature through resistive heating of the reactor. InN nanoparticles were directly grown over TiO₂ nanoparticle films in the reactor using TMIn and NH₃. TMIn (Strem, > 98 % purity) was transferred to a stainless-steel tube after vacuum distillation; it was introduced to
the reactor with a small flow of He (99.9995 %) carrier gas via a stainless-steel ring (diameter 3 mm) perforated with small holes to provide a homogeneous flow onto the substrate. The distance between the TiO₂ film and the TMIn outlet is adjustable and was typically set at ~1 cm. The flow rate of TMIn was adjusted with a needle valve. A flowing gas mixture of NH₃ in He, subjected to microwave discharge (800 W), was introduced upstream of the gas flow to the reactor and served as the source of nitrogen. Flow rates of NH₃ and He were controlled with mass-flow controllers (MKS, model 1179 MFC) that were calibrated before and after experiments with a wet-test meter and, for smaller flows, through the pressure increase in a calibrated volume.

Figure 1: Schematic diagram of the experimental system for plasma-enhanced chemical vapor deposition (PECVD).

Before deposition of InN, the TiO₂ film was cleaned with an oxygen plasma at 523 K for 30 min. Typical experimental conditions were: total flow rate $F_T = 60$ STP cm³ s⁻¹ (STP denotes 1 atm and 273 K), flow rate of TMIn (820 ppm in He) $F_{TMIn} = 2–10$ STP cm³ s⁻¹, flow rate of NH₃ $F_{NH₃} = 20$ STP cm³ s⁻¹, total pressure $P = 5.2$ Torr, reaction temperature $T = 358–623$ K, duration of deposition $t = 15–120$ min.
Absorption spectra were recorded with a spectrophotometer (Jasco, model V–570). For photosensitization tests, the devices were assembled in a sandwich configuration with the TiO$_2$ film facing a Pt counter electrode, prepared on electron-beam deposition of a layer of Pt (thickness 200 nm) onto a FTO conducting glass. A film (Parafilm, $5 \times 10$ mm$^2$), on the periphery of the edge of the cell and placed between the Pt electrode and the TiO$_2$ film, served as a spacer for the electrolyte, producing an active area $\sim 0.5$ cm$^2$. The redox electrolyte solution comprised I$_2$ (0.3 M) and LiI (0.03 M) in propylene carbonate.

The solar cell was illuminated with a commercial solar simulator (Yamashita-Denso, model YSS–50A); its light intensity (or radiant power) was adjusted with a Si solar cell to simulate AM 1.5 solar radiation. Current–voltage ($J–V$) measurements were undertaken using a digital meter (Keithley, model 2440). The incident photocurrent conversion efficiency (IPCE) measurements were measured with a monochromator (Dongwoo Optron, model DM150i). A digital multimeter (Keithley, model 2400) was used to measure the photocurrent response from the sample.

Results and Discussions

InN on TiO$_2$ nanoparticles: Figure 2 shows a comparison of UV–vis spectra of TiO$_2$ and InN/TiO$_2$ films with various periods of deposition. Major absorption by a pure TiO$_2$ film occurs from 390 nm into the UV region. The spectra of InN/TiO$_2$ films show a pronounced broad absorption in the UV–vis range; the
absorption shifts to the red as the duration of deposition increases. The InN/TiO₂ film after deposition for 120 min shows significant absorption in the range 390–900 nm, similar to Grätzel’s black dye.² This result indicates InN to be a suitable absorber of sunlight, confirming the observation recently made by Wang and Lin.²

![Figure 2. UV–vis spectra of a TiO₂ film (solid line) and InN/TiO₂ films with various durations of deposition. The spectrum is normalized at 350 nm. Deposition temperature 358 K; total pressure 5.2 Torr; flow rate of TMIn (820 ppm in He) = 6 sccm; flow rate of NH₃ = 20 sccm; duration of deposition: 30 min (short dashed line), 60 min (dotted line), 90 min (long dashed line), 120 min (dashed-dotted-dotted line).]

We examined systematically the dependence of the photoelectrical behavior of InN-sensitized TiO₂ films on deposition conditions by varying separately the flow rate of the reagents, the temperature of the substrate, and the duration of deposition. The devices for analysis were illuminated with AM
Figure 3. Dependence of efficiency ($\eta$) of power conversion on (A) substrate temperature, (B) flow rate of TMIn (820 ppm in He), and (C) duration of deposition.

1.5 solar radiation at 100 mW cm$^{-2}$. Figure 3 indicates the relations between the efficiency ($\eta$) of power conversion and deposition conditions. This efficiency, ranging $\sim$0.14–0.20 %, generally increases with the size of InN particles; it thus increases as the deposition temperature is decreased, as the flow rate of TMIn is increased, or as the duration of deposition is increased. These trends approach a limit within a small range of experimental conditions, as shown in Figure 3. Based on this result, the best temperature for InN deposition of the TiO$_2$
substrate is below 423 K. Figure 4 shows SEM images of a side view of the InN/TiO₂ films. It is clear that only the surface layer of TiO₂ was coated with InN, the inner layer of TiO₂ film was uncoated. It appears that, in the PECVD process, the holes between TiO₂ nanoparticles on the surface layer were filled readily with InN and blocked the deposition of the inner layers, especially at a higher concentration or greater flow rates of TMIn. Under such conditions, the inner layer of TiO₂ film was not coated with InN; the efficiency therefore rapidly approached a limit at which the surface TiO₂ was coated with InN and a greater flow rate of TMIn or a greater duration of deposition provide no further contribution to the sensitization.

Figure 4. SEM images of a side view of InN/TiO₂ films. Deposition temperature 358 K; total pressure 5.2 Torr; flow rate of TMIn (820 ppm in He) = 6 sccm; flow rate of NH₃ = 20 sccm. (A) deposition period 30 min, ×7000; (B) same as (A) but with ×50000; (C) deposition period 120 min, ×7000; (D) same as (C) but with ×50000.
We also examined carefully the dependence of the photoelectrical behavior of InN-sensitized TiO$_2$ films on the thickness of the TiO$_2$ film. The open-circuit voltage is independent of the TiO$_2$ film thickness, and the short-circuit current increases by about 25% as the thickness of the TiO$_2$ film increases from 0.7 to 5.9 µm; the thickness of the deposited InN was found to be ~330 nm in these experiments. These results indicate that TiO$_2$ has some contribution to the conversion efficiency and decreasing the thickness of uncoated TiO$_2$ does not increase the conversion efficiency, suggesting that charge recombination in the uncoated TiO$_2$ layer might not be the major factor limiting the efficiency of the film under present conditions.

Figure 5 presents a typical IPCE spectrum of TiO$_2$ and InN/TiO$_2$ films. All three InN/TiO$_2$ films show photocurrent responses below 550 nm in contrast with the TiO$_2$ film that responds only in the UV range ($\lambda < 390$ nm). Furthermore, with increasing period of deposition, the IPCE values of InN/TiO$_2$ films at longer wavelengths increase. This phenomenon is consistent with that indicated in the UV–vis absorption spectrum, but the IPCE decays rapidly as the irradiation wavelength increases. A large fraction of carriers are perhaps lost to charge recombination within the particle or at the InN/TiO$_2$ interface. Further improvement on the interface between InN and TiO$_2$ is needed in order to increase the efficiency of power conversion.
Figure 5. IPCE spectrum of a TiO$_2$ film (dotted line) and InN/TiO$_2$ films with various durations of deposition. Deposition temperature 358 K; total pressure 5.2 Torr; flow rate of TMIn (820 ppm in He) = 6 sccm; flow rate of NH$_3$ = 20 sccm. Deposition periods: 30 min (dashed line), 60 min (solid line), and 120 min (dashed-dotted-dotted line).

Figure 6 indicates the current–voltage ($J–V$) character of a reference TiO$_2$ film and our most efficient InN-sensitized TiO$_2$ sample. The measurements under simulated AM 1.5 sunlight illumination at 100 mW cm$^{-2}$ indicate an open-circuit voltage $V_{OC} = 611$ mV and a short-circuit current $J_{SC} = 0.688$ mA cm$^{-2}$, with an efficiency $\sim$0.24% of power conversion and a filling factor $ff = 0.58$. A reference sample of uncoated TiO$_2$ indicates that the photocurrent density generated is much smaller than that of samples sensitized with InN nanoparticles, consistent with InN nanoparticles being efficient sensitizers for nanocrystalline solar cells based on TiO$_2$. The sample was irradiated under AM 1.5 solar illumination at 100 mW cm$^{-2}$ for 5 h with no apparent decrease in its performance, indicating the robustness of this inorganic sensitizer.$^3$ Comparing with the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{ipce_spectrum}
\caption{IPCE spectrum of a TiO$_2$ film (dotted line) and InN/TiO$_2$ films with various durations of deposition. Deposition temperature 358 K; total pressure 5.2 Torr; flow rate of TMIn (820 ppm in He) = 6 sccm; flow rate of NH$_3$ = 20 sccm. Deposition periods: 30 min (dashed line), 60 min (solid line), and 120 min (dashed-dotted-dotted line).}
\end{figure}
parameters \(V_{OC} = 350\, \text{mV}, J_{SC} = 1.8\, \text{mA cm}^{-2}, f = 0.48,\) efficiency = 0.3 % of an InAs-sensitized TiO\(_2\) nanocrystalline solar cell fabricated by Nozik and coworkers as alluded to in the Introduction, our InN-sensitized TiO\(_2\) solar cell has comparable values of \(V_{OC}\) and \(f\), with a somewhat smaller \(J_{SC}\). This condition indicates that we must improve the contacts to the electrodes and the efficiency of electron transfer, and suppress the charge recombination to improve the conversion efficiency. Optimization of the particle surface, the amount of TiO\(_2\) coated with InN and the electrolyte recipe, and finding a good linker between InN and TiO\(_2\) are expected to increase further the efficiency.

Figure 6. \(J-V\) characteristics of a TiO\(_2\) film (dashed line) and an InN/TiO\(_2\) film (solid line) under AM 1.5 illumination at 100 mW cm\(^{-2}\). The photovoltaic parameters are \(V_{OC} = 611\, \text{mV}, J_{SC} = 0.688\, \text{mA cm}^{-2}, f = 0.58,\) and power conversion efficiency = 0.24 %. Deposition temperature 358 K; total pressure 5.2 Torr; flow rate of TMIn (820 ppm in He) = 8 sccm; flow rate of NH\(_3\) = 20 sccm; duration of deposition=2 h.
Conclusions
InN has been deposited onto a porous nanocrystalline TiO$_2$ substrate by means of plasma-enhanced chemical vapor deposition using trimethyl indium and ammonia as sources of indium and nitrogen, respectively. The sensitized InN/TiO$_2$ solar cell exhibits a performance similar to that reported for a nanocrystalline TiO$_2$ solar cell sensitized with InAs quantum dots; the photovoltaic parameters are $V_{OC} = 611$ mV, $J_{SC} = 0.688$ mA cm$^{-2}$, $ff = 0.58$ and efficiency $= 0.24$ % of power conversion, determined using an AM 1.5 solar simulator at 100 mW cm$^{-2}$. The performance of the solar cell may be improved with further modification and optimization. With an improved efficiency, the robust physical-chemical properties of the InN/TiO$_2$ system may afford the possibility of providing a low-cost photo-electrode for applications in solar energy conversion or water splitting.

References:
2. InN/TiO₂ nanoparticles by OMCVD (T. T. Wang and M. C. Lin): TiO₂ sol gel was obtained from the acid-type reaction of i-Propanol and titanium isopropoxide developed by INER. Size well controlled to 20 nm TiO₂ nanoparticles were formed by 12hr 503K autoclaving and kept in hood to avoid light exposure before use. We first prepared the anti-reflection layer by spin coating TiO₂ sol-gel over conducting glass (FTO, fluorine-doped SnO₂) which may reduce the incident light loss during direct illumination. Layered anatase TiO₂ was screen-printed over anti-reflection layer in thickness of 2µm after 30 min baking at 723 K. After that the TiO₂ substrates were immersed in 0.1M TiCl₄ (aq) at 343K for 30 min to improve the “bridging” between separated nanoparticles. Finally, this bridging was solidified after 2 min 500 W microwave treatment, spinel shapes TiO₂ (Figure 7(A)) were formed between ordinary round nanoparticles. This modified buffer layer may improve the electron transfer efficiency greatly.

Among the InN deposition studies, the most efficient precursor of In was trimethyl-indium ((CH₃)₃In) which was purchased from Aldrich without any purification before use. The most used N source was hydrogen azide (HN₃) which was synthesized from reaction of sodium azide and phosphoric acid. The HN₃ product was purified by freeze-pump-thaw cycle under a hood to remove water and kept in an ethanol-dry ice mixture bath with extremely caution before use.

The deposition of InN was made with a homemade OMCVD system, The vacuum chamber was evacuated to lower than 2x10⁻⁷
torr and baked to 383 K before deposition taking place. During deposition, TiO₂ substrate was heated by thermal radiation from tungsten wire to a desired temperature. Then TMIn and HN₃ were introduced into the vacuum chamber simultaneously. The pressure of the reactant was HN₃: TMIn=1×10⁻⁵:2×10⁻⁶ tore. The TMIn/HN₃ ratio was kept at 1/5. After deposition time (2-120 min), the substrates were annealed at 723 K to reduce crystalline defects.

Fabrication of our InN/TiO₂/FTO solar cell is similar to the TiO₂ based DSSC. The devices were assembled in a sandwich configuration with InN/TiO₂/FTO photoanode facing a counter Pt electrode. The semi-opaque counter Pt electrode was made by using e-gun to vaporize Pt and condense the Pt particles on ITO glass with thickness as 20 µm. An enclosed spacer filled with I⁻/I₃⁻ electrolyte with volume ~8 mm³ was insert between Pt and TiO₂ electrode. The electrolyte was 0.3M 1,2-Dimethyl-3-propylimidazolium iodide, 0.03M I₂ and 0.5M t-butyl pyridine in 3-methoxypropionitrile.

To measure solar cell efficiency, we set up an YSS-50A AM1.5 solar simulator which has a good solar spectral output and light intensity stability at 100 mW/cm² solar radiation. The Keithley sourcemeter 2440 was used in J-V curve measurement. Light intensity was calibrated by using Gentec SOLO PE power meter coupled with UP19K-15S-H5 Si photodetector head. For our rugged surface substrates, we take the absorption spectra in the Integrating Spheres to avoid the undesirable diffraction interference.
Results and Discussion:

In Figure 7, we present the high resolution SEM morphologies of (A) modified 15-20nm TiO$_2$ nanoparticles, grown InN on TiO$_2$ after (B) short time and (C) ~ (F) long time deposition. After 2hr deposition in our low pressure OMCVD system, significant InN particles were observed and no indium droplets formed on the surface for operating temperature above 583 K. The averaged InN particle size is estimated to be 15, 30, 90 and 150 nm at operation temperature of 583, 623, 673 and 723 K, respectively. It is clear to see that InN wraps up Ti(OH)$_4$-modified spinel
shape TiO$_2$ nanoparticles, and ball-like corpuscles are formed at $T< 623$ K deposition in contrast to the giant particle grown “above” TiO$_2$ surface at high temperature. The loose contact between InN and TiO$_2$ for the high temperature sample implies the electron transfer is unfavored in optoelectronics applications.

Figure 8. XRD spectrum of InN/TiO$_2$/FTO after 2hr CVD deposition at (A) 673 K (B) 533 K. (■Anatase TiO$_2$ ●SnO$_2$ ▲InN)

In Figure 8 X-ray diffraction studies, three group peaks are observed including: anatase TiO$_2$, SnO$_2$ for FTO conducting glass and InN particles. In contrast to the low deposition temperature sample which lacks crystallinity, several orientations (100), (002) and (101) of InN are observed for the samples above 673 K reveal that polycrystalline InN is deposited on anatase TiO$_2$. Amorphous sample can be re-crystallized and morphologies are greatly improved by annealing at 723 K. The deposited InN possesses two strongest peaks of (002) and (101) which are also the most observed orientations of the InN films on different substrates in previous OMCVD experiments. The stoichiometrical ratio was examined by EDX analysis (see Table
1), indium to nitrogen ratio was kept steadily around 0.7 at T>623K, indicating nitrogen rich-films.

Figure 9. Quantum efficiency of InN/TiO$_2$ system at different temperature (A) 723K (B) 673K (C) 623K (D) 583K with deposition time of 2min (solid) 20min (dash) and 120min (dot).

Figure 9 shows systematic analysis of J-V diagram at different temperature by varying deposition time from 2 to 120 min with incident light as 100 mW/cm$^2$ and exposure area of 0.4 cm$^2$. It is clear to see that both the $J_{sc}$ and $V_{oc}$ drop a lot at higher deposition temperature and longer deposition time. Energy lost with grown crystalline defects could explain the short time deposition sample which possesses the highest conversion efficiency at any given temperature. For the high temperature CVD sample, electron transfer is limited due to loose contact between InN and TiO$_2$ which is reflected by its poor efficiency. Among all, the best quantum efficiency obtained is about 0.21%
after 2 min deposition at 583K. To further study the electron transfer process in our InN/TiO₂/FTO system, we reduce the incident light intensity by placing a neutral density filter which has a flat spectral response curve from 250 nm~2000 nm. The attenuated light intensity is carefully calibrated by a Si photodetector. We found that the photo-current efficiency increased from 0.21% to 0.35 and 0.41% when the incident intensity were reduced to 20 and 9mW cm⁻² (Figure 4), respectively. With a little bit drop in Vₐₑ (from 0.575 to 0.55V), the photocurrent intensity increase twice while the incident light reduces to 1/10 of the one sun-condition. This phenomenon had been discussed among the studies employing cobalt complexes as redox couple relays in DSSC and InAs QDSSC and Na₂S as electrolyte in CdSe QDSSC. The limiting factors of current decrease under high incident light intensity may be: (i) mass transport limitation of redox pair and (ii) the enhancement of charge recombination of electron in TiO₂ and holes in QDs for QDs type solar cell. The limitation of redox pair might be overwhelmed by using a higher concentration electrolyte. However, in our study, in comparison of J-V curve obtained with 0.01M and 0.005M iodine concentration in electrolyte, both show that fill factor increases from 0.6 to 0.77 under lower incident light intensity, which means the alternation in redox couples is no longer the limiting factor. Thus, the decreasing photocurrent might be due to that: the electron transport is restricted by enhancement of back-charge- recombination of electron and hole pair under a high incident light.
Figure 10. Quantum efficiency of InN/TiO$_2$ system at different incident intensity 100(dot), 20(dash) and 9mW/cm$^2$ (solid).

Table 1. EDX analysis of atomic ratio of InN/TiO$_2$/FTO substrate.

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<th>%</th>
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<td>In/N ratio</td>
<td>0.71</td>
<td>0.66</td>
<td>0.75</td>
<td>3.26</td>
<td>-</td>
</tr>
</tbody>
</table>

For the DSSC or QDSSC, the absorbing molecules were chemisorbed by immersing TiO$_2$ substrate in “absorber” dye molecules or QDs solution. Thus, a highly porous structure and multi-layered nanocrystalline TiO$_2$ film will improve the photo efficiency by accommodating more absorbers. The grown InN nanoparticles showed better adhesion on TiO$_2$ surface than the weak chemical adsorption of absorbers. And InN/TiO$_2$/FTO system shows a great stability in conversion efficiency by reassembling the departed device tested weeks ago. However, the
direct deposition restricts InN particles in the very superficial layer of TiO$_2$. Thus the total efficiency is rather limited to date. To overcome this drawback, alternative InN growth methods are carried out in our group.

Conclusion:
In this work, we studied InN deposition on anatase TiO$_2$ nanoparticles at different temperatures by the reaction of TMIn and HN$_3$ using low pressure OMCVD. The averaged InN particles sizes are ranging from 15 to 20 nm for depositions at different temperatures. After annealing at 723 K, crystallized InN can only be grown by T > 583 K deposition. In the AM1.5 measurement, among all the devices, photo-efficiency 0.41% had been achieved under low intensity 9 mw/cm$^2$ illumination. The efficiency decreases to 0.21% under one-sun illumination. This is probably due to the enhancement of recombination of electron hole pairs. Further modification and optimization of the InN/TiO$_2$ system are expected in the next phase of studies.

3. The effects of anchoring groups – the linker between InN and TiO$_2$ (C. K. Wang and M. C. Lin)
We have carried out a series of studies on the effects of the linker or anchoring group between InN and TiO$_2$. Initially we employed the –OX(O)O- linker (X=B and P) by dipping the TiO$_2$ nanoparticle films, prepared by the sol gel method as described in sections (1) and (2), into the solution of H$_3$BO$_3$ and H$_3$PO$_3$ of varying concentrations.
InN deposition onto the treated films by PECVD after drying at about 100°C in the deposition system under vacuum. Before turning on the microwave, the film was first dosed with TMIn to facilitate the formation of the first-layer chemical bond:

\[(\text{CH}_3)_3\text{In} + \text{HOX(O)O-TiO}_2 \rightarrow (\text{CH}_3)_2\text{InOX(O)O-TiO}_2 + \text{CH}_4 \ (\text{g})\]

where X=B or P and the HOX(O)O-TiO$_2$ has been shown by our quantum calculations using VASP to be the key products of the X(OH)$_3$ dissociative adsorption on TiO$_2$ anatase and rutile surfaces.

Following the TMIn dosing and pumping, the substrate was heated to 150°C for PECVD of InN using NH$_3$ and TMIn as we previously reported to INER and in section (1). After PECVD, the fabricated InN/OX(O)O-TiO$_2$ devices were constructed for solar cell operations. The results summarized in Figure 11 clearly demonstrates that the electron-withdrawing B-element enhances, whereas the P-linker, diminishes the photo-efficiency.

This is a very important finding as both strongly binding linkers (to TiO$_2$ with >100 kcal/mol binding energies) can be used for other semiconductor quantum dots, for example, Si (using SiR$_4$), CdSe (using Cd(CH$_3$)$_2$), etc., as precursors to bind with HOX(O)OTiO$_2$. 


The effects of H$_3$BO$_3$ and H$_3$PO$_3$ as anchoring groups on photocurrent of InN/TiO$_2$.

Quantum chemical calculations to account for the observed B- and P- effects are under way.


We attempted to prepare TiO$_2$ nanorods by the direct oxidation Ti foils as described Peng et al. 1 We washed titanium foils with distilled water and acetone in ultrasonic cleaner in 10 min. before employing hydrochloric acid (80°C, 30 wt%) to etch oxidized layer on surface of titanium foil. Subsequently, we removed residual hydrochloric acid on titanium foils with distilled water before putting the cleaned titanium foils into our reaction system.

The reaction system consists of two parts (see Figure 12): (1) a gas inlet for two different gases, He carrier gas and oxidant gas. (2) a quartz reaction tube of 5 cm diameter. The quartz tube was heated by a furnace with temperature up to 850 °C, followed by passing
various oxidants into the tube to oxidize Ti foil and produce TiO$_2$ nanorods (see Figure 13). After oxidation, the film of TiO$_2$ nanorods was deposited with InN by PECVD, as described in section (1).

![Figure 12: Schematic diagram of the Ti foil oxidation system.](image)

![Figure 13: SEM images of TiO$_2$ nanorods prepared by flowing ~0.3 Torr 2-propanol and ~75 sccm of He into quartz reaction tube at 850°C for 2 h. The lengths of nanorods are ~2–3 μm and the diameters are ~100 nm.](image)

The photo-efficiency of the InN/TiO$_2$-nanorod device, which is dominated by TiO$_2$ rutile structure, is relatively low at present. Currently we are exploring the effects of nanorods’ height and
spacing as well as the type of the HOY(O)O- (Y=B and P) linkers, on the overall efficiency. This work is still in its infancy, we expect the technique to be able to fabricate a robust InN/TiO₂ photo-electrode for potential water-splitting applications.

References:
參、主要發現與結論

在這一年利用 PECVD (NH₃+TMIn) 及 OMCVD (HN₃+TMIn) 的實驗結果，與目前 NREL 之 Nozik 實驗室在 2006 年發表的 InAs/TiO₂ 結果很接近（見下圖）：

\[ J. \text{Phys. Chem. B} \ 2006, \ 110, \ 25451 – 25454 \]

Nanocrystalline TiO₂ Solar Cells Sensitized with InAs Quantum Dots†

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We report nanocrystalline TiO₂ solar cells sensitized with InAs quantum dots. InAs quantum dots of different sizes were synthesized and incorporated in solar cell devices. Efficient charge transfer from InAs quantum dots to TiO₂ particles was achieved without deliberate modification of the quantum dot capping layer. A power conversion efficiency of about 1.7% under 5 mW/cm² was achieved, this is relatively high for a nanocrystalline metal oxide solar cell sensitized with presynthesized quantum dots, but this efficiency could only be achieved at low light intensity. After one sun, the efficiency decreased to 0.3%. The devices are stable for at least weeks under room light in air.

(A)

(B)

InN/TiO₂ 與 InAs/TiO₂ 目前結果的比較：(A) Nozik 等 2006 年 InAs/TiO₂ 論文的摘要，(B) InAs 與 InN 的光電效率比較。

吾人利用高溫 PECVD 及 OMCVD 所製成的 InN/TiO₂ 當然比 Nozik
等利用水溶液低溫物理吸附、並有化學毒性的 InAs/TiO$_2$ 系統在物性與化性上均好得很多。此兩種量子點太陽能系統目前效率不高的原因至少有二：(1)依前述 SEM 分析結果，InN 或 InAs 量子點無法如有機染料分子一樣進入 TiO$_2$ 奈米薄膜的內部孔洞，因此量子點濃度不高，(2)量子點(InN 或 InAs)與 TiO$_2$ 奈米粒子表面尚未有良好、有效傳遞電子的化學鍵(諸如染料分子所用的-C(O)O-鍵)。

為解決上述第 (2) 點，吾人已在-OY(=O)O-，Y=B 或 P，接鍵的實驗結果發現，-OB(O)O- 與 TiO$_2$ 連接對光電流有明顯的幫助，但同樣能與 TiO$_2$ 強力接連的-OP(O)O-鍵則有明顯的負作用，這是非常重要的實驗結果，因為-OB(O)O- 能與其他很多的半導體量子點，諸如 InP, Si, CdSe 等等，利用化學反應接連在 TiO$_2$ 奈米點薄膜上。

有關以上第 (1) 點的改善，目前已在兩方面進行：(A) 直接利用 Ti-foils 製作 TiO$_2$ nanorods (如 section (4) 所述)，達成廣大的孔洞；(B) 利用 glycine nitrate 的方法在 TiO$_2$ 奈米薄膜的上層製作大孔洞。同時在 TiO$_2$ 奈米粒子中加入 n-或 p- dopants 的實驗已進行中，此外，半導體敏化的量子點本身亦可加入 n-或 p-dopants，諸如 Zn 或 Sb 等。

吾人確信將來在敏化量子點(sensitizer)、量子點與 TiO$_2$ 奈米粒子的接連化學鍵 (linker or anchoring group) 及 TiO$_2$ 奈米薄膜的 n-或 p-doping 三方向的調製與改進，一定可以製作一個高效率的 In(M)N/Linker/d-TiO$_2$ 系統 (M=Zn, Ga, Sb…；Linker = OY(=O)O, Y= B, P, Si, Al…；d= n- or p-dopants)，以供太陽光水分解之應用。


5. M.-C. Wu and C.-S. Lee, “A New Deposition to Prepare a Thin Film of Quasi-Aligned-MoO₃ Nanorods”, Submitted to Thin Solid Films