行政院國家科學委員會專題研究計畫　期中進度報告

高效率光電轉換用自身組織功能性奈米結構材料與元件之前瞻研究(1/3)

計畫類別：整合型計畫
計畫編號：NSC94-2120-M-009-013-
執行期間：94 年 10 月 01 日至 95 年 11 月 30 日
執行單位：國立交通大學材料科學與工程學系(所)

計畫主持人：韋光華
共同主持人：謝嘉民，鄭有舜，黃中垚，林建村

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
國際合作計畫研究心得報告
處理方式：本計畫可公開查詢

中　華　民　國 95 年 6 月 12 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）

- 計畫主持人及執行機構：
  韋光華教授　(Principal Investigator: Professor Kung-Hwa Wei)
  交通大學材料系 (Dept. of Materials Sci. & Eng., National Chiao Tung University)

- 共同主持人及執行機構：
  ・林建村教授　(Co-Principal Investigators: Professor Jiann-T'suen Lin)
  中央研究院化學所　(Institute of Chemistry, Academia Sinica)
  ・黃中垚教授　(Professor Jung Y. Huang)
  交通大學光電所　(Dept. of Electro-Optics, National Chiao Tung University)
  ・謝嘉民博士　(Researcher Jia-Min Shieh)
  國家實驗研究院國家奈米實驗室　(National Nano Device Laboratories)
  ・梁耕三主任　(NSRRC director Keng S. Liang)
  國家同步輻射研究中心　(National Synchrotron Radiation Research Center)
  ・鄭有舜博士　(Researcher U-Ser Jeng)
  國家同步輻射研究中心　(National Synchrotron Radiation Research Center)

研究題目：高效率光電轉換用自身組織功能性奈米結構材料與元件之前瞻研究
(Project Title: Frontier Research on Self-assembled Functional Nanostructured Materials and Devices for High Efficiency Optoelectronics Applications)

全程計畫執行期限（Project Period）：
2005 年 8 月 1 日至 2008 年 7 月 31 日
Three years from 2005/08/01 to 2008/07/31

分年經費（Budget for each year）：
第一年 First year　（2005/08/01～2006/07/31）:10,000,000　NT Dollars
第二年 Second year（2006/08/01～2007/07/31）: 10,000,000　NT Dollars
第三年 Third year　（2007/08/01～2008/07/31）: 10,000,000　NT Dollars

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

The main objective of this project is to build a high-efficiency nanorods- conjugation polymer heterojunction photovoltaic cell that incorporates ordered and bandgap-engineered nanorods and dye-tethered conjugated polymers. The principal idea behind this photovoltaic cell design is to form heterojunctions between the ordered nanorods and conducting conjugated polymers in such a way that the inter-rod distance is on the order of the diffusion length of excitons.

Three different approaches will be taken to construct the inner composite films within the photovoltaic cell.

The first approach begins by incorporating metal ions selectively into the polar block of a diblock copolymer through ionic-polar interactions. Then, the metal ions in the block order into metal oxide seeds after thermal annealing. O_2 plasma treatment was used to remove the polymer template. The metal oxide molecules then crystallize on the metal oxide seeds to form metal oxide nanorods. Subsequently, conducting polymer will be spin-coated onto the substrate containing these nanorod arrays to form the

composite film.

The second approach involves deposition a thin film of oxide, and then spin-coating a thin layer of conducting-coil diblock copolymer for forming periodic domain. After UV treatment or solvent etching, the coil domains are removed, and periodic nanoporous film template can be obtained. Using solution or chemical vapor deposition methods to grow nanorods in the nanpores of the film.

The third approach is concerned with an inorganic/organic nanocomposite structure. By providing strong interactions between the surface ligands on nanorods and the polymer segment of n-type block in a conjugation p-n type diblock copolymer, we can sequester the nanorods into the n-type block while the p-type block will serve as the matrix. Thus, a simpler but more random structure can be obtained.

After the construction of the composite films, electrodes will be deposited by sputtering techniques. The optical and physical properties of these nanorods- conducting polymer nanocomposites will be measured and the efficiency of photo-to-current conversion will be studied.

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

Faculty:

Kung-Hwa Wei (professor)
(Dept. of Materials Sci. & Eng., National Chiao Tung University)
Jiann-T'suen Lin (professor)
(Institute of Chemistry, Academia Sinica)
Jung Y. Huang (professor)
(Dept. of Electro-Optics, National Chiao Tung University)
Jia-Min Shieh (researcher)
(National Nano Device Laboratories)
Keng S. Liang (director)
U-Ser Jeng (researcher)
(National Synchrotron Radiation Research Center)
Jeng-Tzong Sheu (professor)
(Institute of Nanotechnology, National Chiao Tung University)

Student:

(Dept. of Materials Sci. & Eng., National Chiao Tung University)
Chung-Ping Li, Chia-Hung Chou, Ching-Mao Huang, Mao-Yuan Chiu, Hsu-Shen Wang, So-Lin Hsu, Guan-Yu Chen, Chia-Hao Wu (Ph.D. students),
Chen-Ping Chen (M. S. student), Dhanasekaran Manickam (Post Doc.)

4. Please list at most six most important publications after your project has started for six months. (Project starts on Aug. 1, 2005)

- Chung-Ping Li, Siao-Wei Yeh, Han-Chang Chang, Jung Y. Huang, and **Kung-Hwa Wei***, "The Orientation of CdSe Nanorods Affects the Electron Mobility of CdSe/P4VP Nanodomains Self-Assembled within a Poly(styrene-*b*-4-vinylpyridine) Diblock Copolymer Thin Film", *Small* **2**, 359, **2006 (starts at 2005, no Impact Factor until 2007)**

- Chung-Ping Li, Chia-Hao Wu, **Kung-Hwa Wei***, Jeng-Tzong Sheu, and Jung Y. Huang, "Collective Electron Transport in Au Nanoparticles Self-Assembled in the Poly(4-vinylpyridine) Nanodomains of a Poly(styrene-*b*-4-vinylpyridine) Diblock Copolymer Thin Film", *J. Am. Chem. Soc.* **2006,** submitted **(SCI IF: 6.903)**

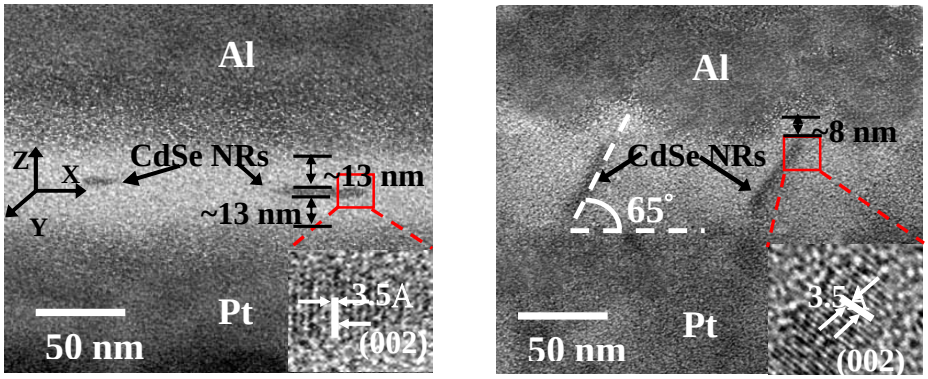
- Chia-Hung Chou, Chen-Ping Chen, So-Lin Hsu, and **Kung-Hwa Wei***, "Blue electroluminescence enhancement of polyfluorene copolymer incorporating side-chain-tethered gold nanoparticles", *Advanced Materials* **2006**, submitted. **(SCI IF: 8.079)**

5. 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)

We have obtained two outstanding results. First, orientation of CdSe nanorods affecting the electron mobility of nanorods / poly(4-vinylpyridine) nanodomains in a poly(styrene-*b*-4-vinylpyridine) was obtained. Second, collective electron transport in Au nanoparticles self-assembled in the poly(4-vinylpyridine) nanodomains of a poly(styrene-*b*-4-vinylpyridine) was revealed.

1. Orientation of nanorods affects the electron mobility of nanorods /polymer nanodomains:

CdSe nanorods (NRs) self-assembled in the poly(4-vinylpyridine) nanodomains of a poly(styrene-*b*-4-vinylpyridine) diblock copolymer thin film were aligned under the influence of the polarization forces created by an applied electric field. Figure 1 shows cross-sectional TEM images of 33% (CdSe NRs/P4VP)-*b*-PS thin films prepared (a) in the absence of and (b) in the presence of an applied electric field. （Small **2,** 359, **2006**）



(a) **(b)**

Figure 1: Cross-sectional TEM images of 33% (CdSe NRs/P4VP)-*b*-PS thin films prepared (a) in the absence of and (b) in the presence of an applied electric field. The insets display the respective HRTEM lattice images of a CdSe NR incorporated within a single P4VP nanodomain of (CdSe NRs/P4VP)-*b*-PS.

Table 1 shows the electron mobilities of the CdSe NRs/P4VP nanodomains in the out-of-plane cases were ca. eight times larger than those in the in-plane cases. In both in the out-of-plane and in-plane cases, the electron mobility increased upon increasing the number of CdSe nanorods.

Table 1: Electron barrier heights (ϕ_e), electron mobilities (μ_0), and field coefficients (E_0) for in-plane and out-of-plane CdSe NRs incorporated within P4VP nanodomains in a PS matrix.

vol% of CdSe in P4VP	In-plane			Out-of-plane		
	$\phi_e \times (m/m^*)^{-1/3}$ (eV)	$\mu_0 \times 10^4$ (cm^2/Vs)	$E_0 \times 10^{-4}$ (V/cm)	$\phi_e \times (m/m^*)^{-1/3}$ (eV)	$\mu_0 \times 10^4$ (cm^2/Vs)	$E_0 \times 10^{-4}$ (V/cm)
33	1.66	1.2	5.8	1.45	9.3	6.2
40	1.54	4.1	5.6	1.35	32.3	5.8
48	1.43	17.6	6.1	1.21	141.5	5.6
55	1.37	31.1	5.9	1.16	248.4	6.3
65	1.29	90.2	5.7	1.05	723.2	5.9

2. Collective electron transport in Au nanoparticles self-assembled in the polymer nanodomains:

Thin films that consisted of Au nanoparticles (NPs) self-assembled in a poly(4-vinylpyridine) nanodomain of poly(styrene-*b*-4-vinylpyridine) diblock copolymer were prepared by polar interaction and solvent selectivity. Figure 2 shows (a) conventional, (b) high-resolution, and (c) cross-sectional TEM images of a thin film of 48% (Au NPs/P4VP)-*b*-PS. From the current–voltage characteristics of these thin films, we found that the collective electron transport behavior of Au nanoparticles sequestered in the spherical poly(4-vinylpyridine) nanodomains was dictated by Coulomb blockade and was quasi one-dimensional, as opposed to the

three-dimensional behavior displayed by Au nanoparticles that had been dispersed randomly in homo-poly(4-vinylpyridine) (Figure 3). （J. Am. Chem. Soc. **2006,** submitted）

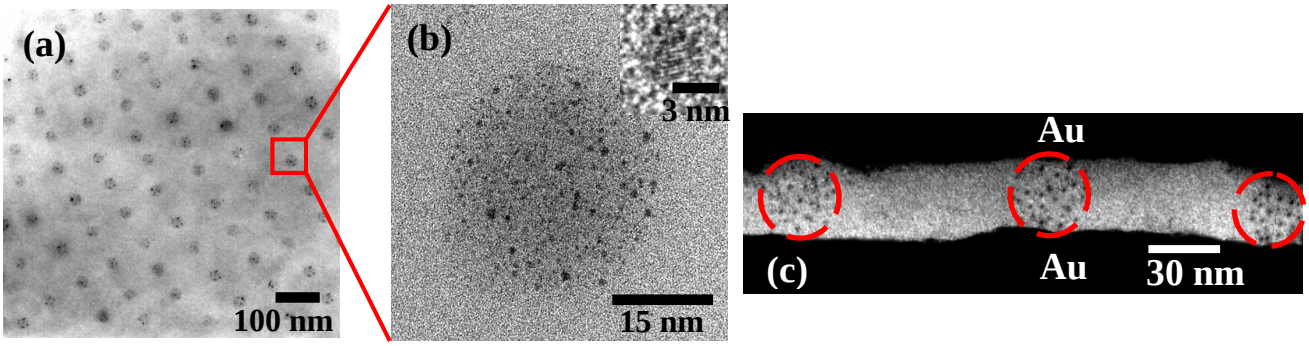


Figure 2: (a) conventional, (b) high-resolution, and (c) cross-sectional TEM images, obtained without staining, of a thin film of 48% (Au NPs/P4VP)-*b*-PS.

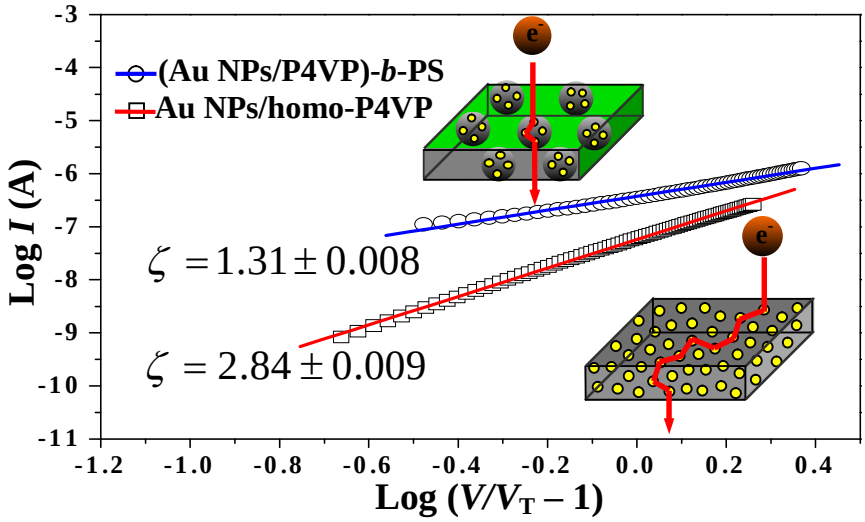


Figure 3: Scaling behavior of the *I–V* curves of 48% (Au NPs/P4VP)-*b*-PS and Au NPs/homo-P4VP at 78 K.

Comparison with other similar works in the world:

Our group achieved in arranging pre-synthesized nanorods in large area out-of-plane two-dimenisional arrays by electric field（Small **2,** 359, **2006**）, which is a break through in nanotechnology. Moreover, this is the first time the nanodomain confined effect on the dimensionality of collective electron transport behavior of metal nanoparticles has been reported in the world （J. Am. Chem. Soc. **2006,** submitted）. This work has great implications on hybrid photovoltaic cell or light-emitting diode applications.

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.

International Symposium on the Manipulation of Advanced Smart Materials, May 26-27, 2005 in Japan.
The 4th Cross-Strait Workshop on Nano Science and Technology, August 22-25, 2005 in China.
3rd Taiwan-Air Force Nanoscience Initiative Workshop, February 9-11, 2006 in Taiwan.
S&T Exchange-Workshop on Nanotechnology, April 18-22, 2006 in Taiwan.