The 3rd Korea-US Nano Forum (April 3-4, 2006)

Block Copolymer Thin Films for New Functional Nanomaterials

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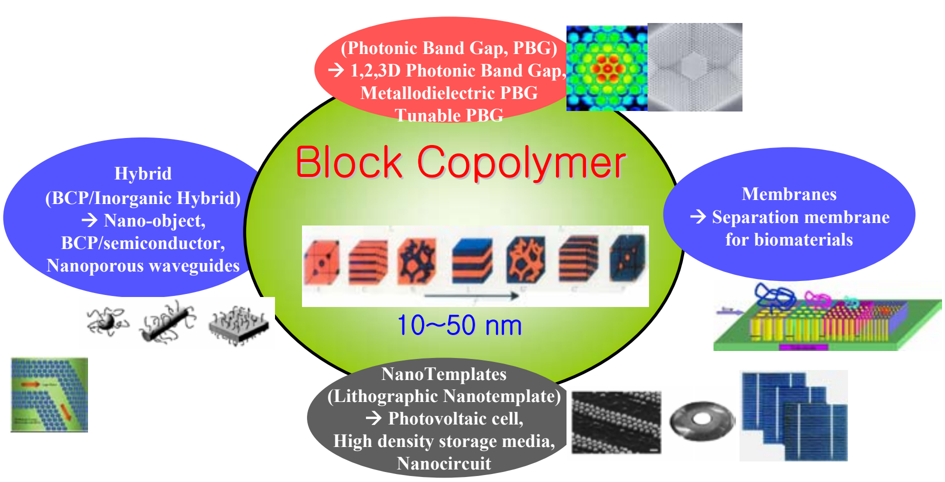
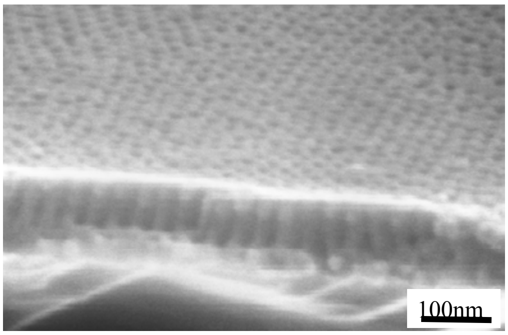
Application of Block Copolymer Thin Films



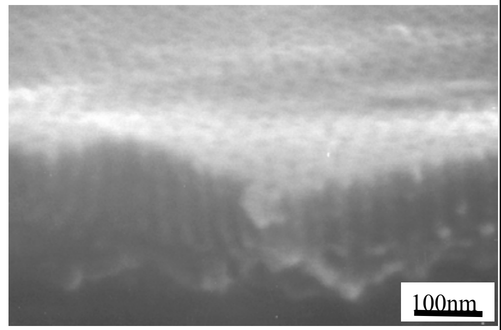
PS-b-PMMA+ PMMA homopolymer

(Kim and Coworkers, Adv. Mater. (2004))

92 nm thickness



273 nm thickness



Annealed at 150°C

Guiding Effect of Homopolymer for the growth of Block copolymer chains perpendicular to the substrate!!

Introduction - Commercial Membrane

Flux

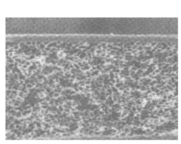
- Pore Area
- Pore Size
- Thickness

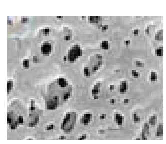
Selectivity

- Pore Size Distribution

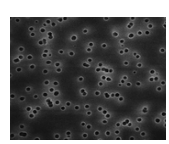
skin layer (0.1-0.5μm) →

Porous Membrnae (50-150μm) →

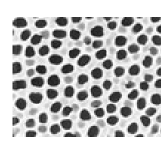




Polysulfone membrane



Track-etched membrane



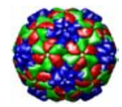
AAO membrane

High flux , Low selectivity

Low flux , High selectivity

Motivation

Human Rhinovirus *Type* 14 (HRV14)



Shape: Dodecagon: Similar to Sphere with
Diameter (nm): Ave : 30.6 Max : 32.4

Separation layer made by Self-assembling block copolymer

- Nanometer-Sized Domain
- Very Thin Thickness
- Narrow Size Distribution

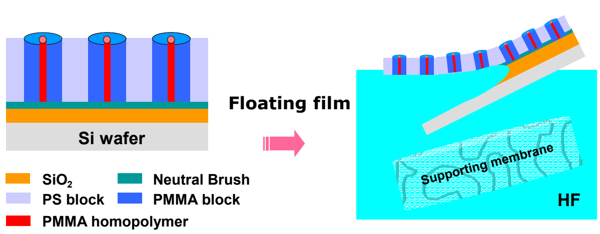
+

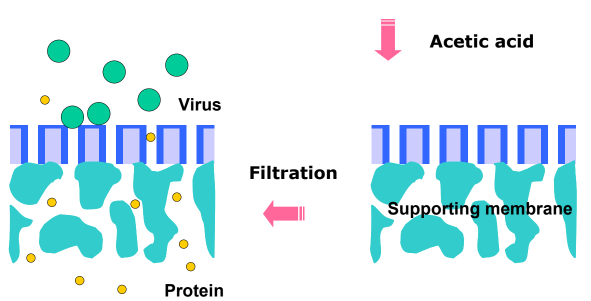
Supporting layer having highly porous structure

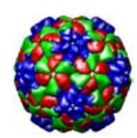
- Facilitation of Flux
- Mechanical Strength

→ ***Nanoporous membrane will show high flux and high selectivity for bio-material separation***

Filtration of Viruses from Proteins





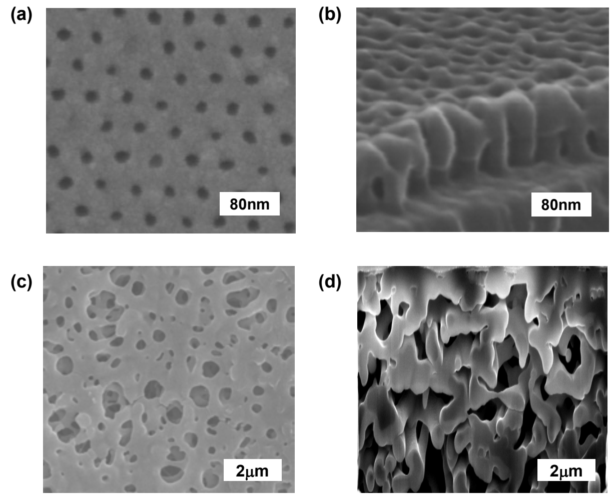


Human Rhinovirus *Type* 14 (HRV14) Diameter : Ave : 30.6 nm Max : 32.4 nm

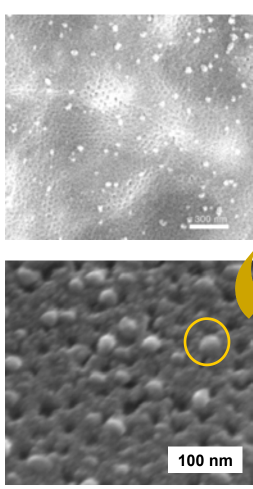
Bovine Serum Albumin (BSA) (Protein)
Diameter: 7.2 nm

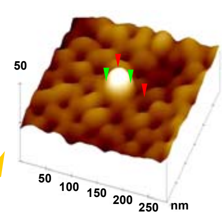
SEM image of membrane (Surface & Cross-section)

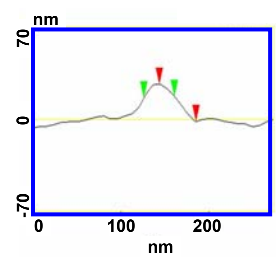
	Top surface	Cross-section
Separation layer (PS-PMMA)	(a)	(b)
Supporting layer (Polysulfone MF Membrane)	(c)	(d)



SEM Image of Membrane Surface After Filtering Virus





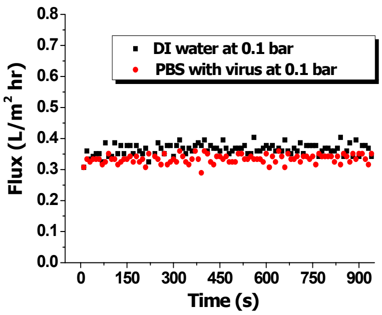


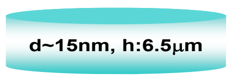
Surface distance	52.354 nm
Horiz distance(L)	41.656 nm
Vert distance	30.596 nm
Angle	36.297 °
Surface distance	41.318 nm
Horiz distance	34.180 nm
Vert distance	0.852 nm
Angle	1.429 °

Shape and size of the particles in the membrane are the same as those of virus (spherical shape & diameter) !!!

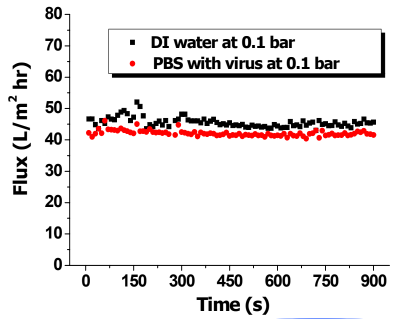
Flux between Conventional Membranes and Nano-membranes

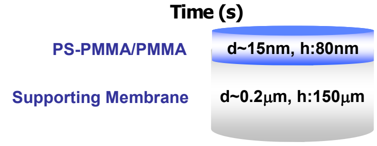
Track-etched Polycarbonate(PC) membrane





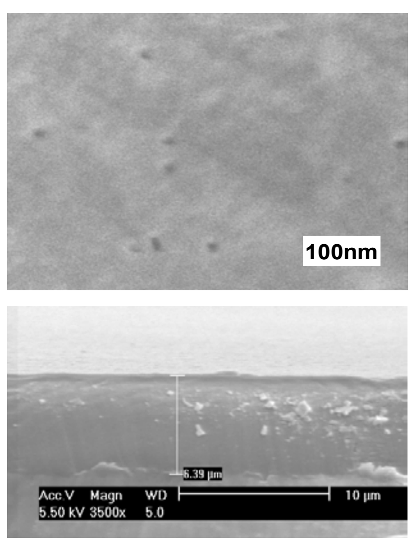
Nano Porous Membranes





Flux of PS-PMMA membrane shows 100 times more than PC membrane due to thin thickness (80 nm) and high surface porosity (20 %) compared to PC membrane (6.5 μm and 2% porosity)

SEM image of PC membrane (Surface & Cross-section)



Surface

Cross-section

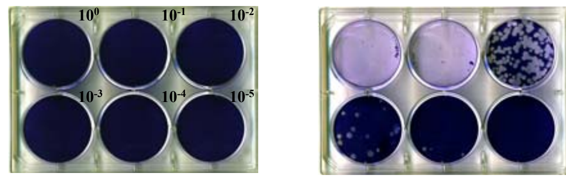
Plaque Assay of Filtrated Virus Solution (conc : 10^6 PFU/5 mL)

Plaque assay

Virus detection method by using infectivity of virus to cell

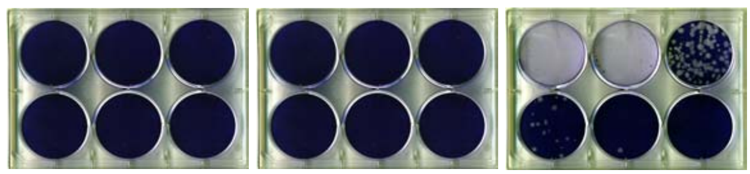
When cells are infected, viruses form plaque.

Negative | Before Filtering (10^6 PFU)



Permeate was diluted by 1 order (0.2ml injected)

PS-PMMA membrane (d~15nm) | Polycarbonate membrane (d~15nm) | AAO membrane (d~20nm)



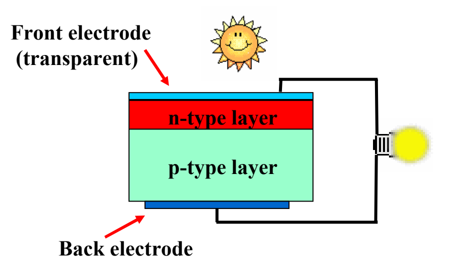
Virus was not detected at filtrated virus solution through PS-PMMA membrane (Kim and coworkers, Adv Mater (2006))

Photovoltaic (PV) Device

Solar cell

Produce electrical energy

Power conversion efficiency



Photodetector

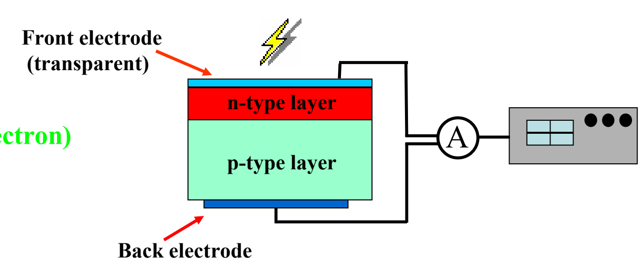
Measure/detect light

Quantum yield

(conversion of photon to electron)

additional external field

improve detection limit



National Creative Research Initiative Center for Block Copolymer Self-Assembly

Organic PV Cells

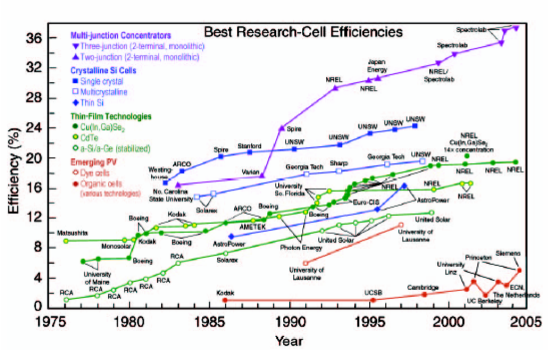


Figure 3. Progress of research-scale photovoltaic device efficiencies, under AM 1.5 simulated solar illumination, for a variety of technologies.

MRS Bulletin, 30, 10 (2005)

PV cells

1. Crystal, Amorphous Si
2. Dye-Sensitized PV
3. Inorganic PV
4. Organic PV

Why Organic?

1. Flexible and Transparent
2. Easy Processing (Roll to Roll Coating)
3. Economic

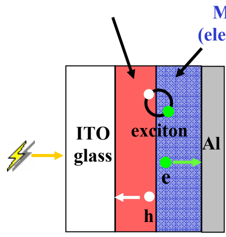
Type

(a) Organic/Organic
(b) Polymer/Organic
(c) Polymer/Polymer

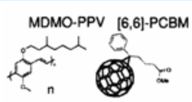
Organic PV Device (Previous Approaches for pn hetrojunction)

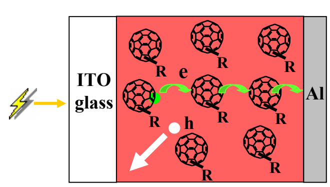
POPT (hole acceptor)
(phenyl-octyl substituted polythiophene)

MEH-CN-PPV
(electron acceptor)



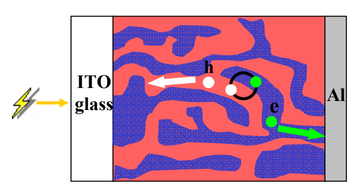
Polymer/Polymer layer
PCE ~ 1.9 %
Friend and coworkers,
Nature, **395**, 257 (1998)



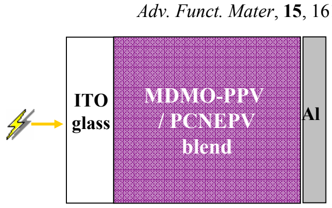


Polymer(P3HT)/PCBM(C60) blend
After heat treatment at 150 °C
PCE ~ 5 %
Heeger and coworkers,
Adv. Funct. Mater, **15**, 1617 (2005)

MEH-PPV / CN-PPV (7:1)
mixture



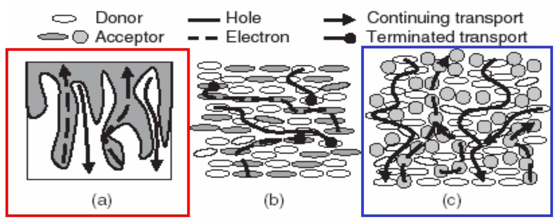
Polymer/Polymer IPN
IPCE ~ 4 % at 550 nm
Friend and coworkers,
Nature, **376**, 498 (1995)



Polymer/Polymer blend
PCE ~ 0.75%
S. C. Veenstra,
Chem. Mater., **2503**, 16 (2004)

Geometry for PN Heterojunction for PV Cells

Ideal Structure

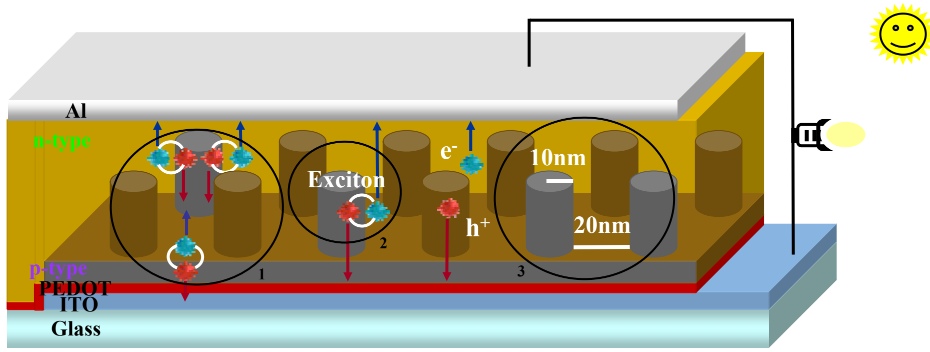


: Similar to IPN structure

Figure 4. Illustrations of different transport scenarios in a donor–acceptor mixture. a) An idealized bulk HJ structure in which segregation of the donor and acceptor molecules leads to an interdigitated structure with lateral-feature sizes no larger than the exciton diffusion lengths. b) No percolating paths across the entire film exist, leading to trapping of the charges (and ultimately, recombination). c) Percolating paths are formed across the film, although the carrier mobility in the mixture is reduced compared to its value in pure films. The nanostructured, spatially distributed donor–acceptor interface is responsible for efficient exciton diffusion in the mixture.

Forrest and coworkers, Adv. Mater, 17, 66 (2005)

Objective: Ideal geometry of PN heterojuction PV device



Key Concepts: 1) Increased p-n junction interfacial area
2) Every exciton can arrive at the interface before disappearance by coupling (Maximum Dissociation)
3) Good path way

Solution: Block Copolymer Templates !!!

Ultra High Density Array of Conducting Polymer Nanowires on ITO glass

Materials

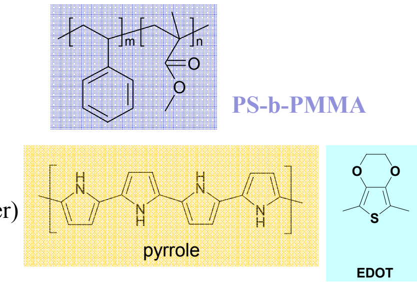
1) Diblock copolymer & neutral brush

PS-b-PMMA (70:30) synthesized by ATRP (Atomic Transfer Radical Polymerization)

: M_n=55,500 PDI= 1.19

PMMA homo polymer (Polymer Source)

: M_n=29,800 PDI= 1.08



PS-b-PMMA

2) Electro-polymerization electrolyte

Pyrrole monomer 99% (Acros) C_4H_5N

EDOT (3,4-Ethylene Dioxythiophene) (Bayer)

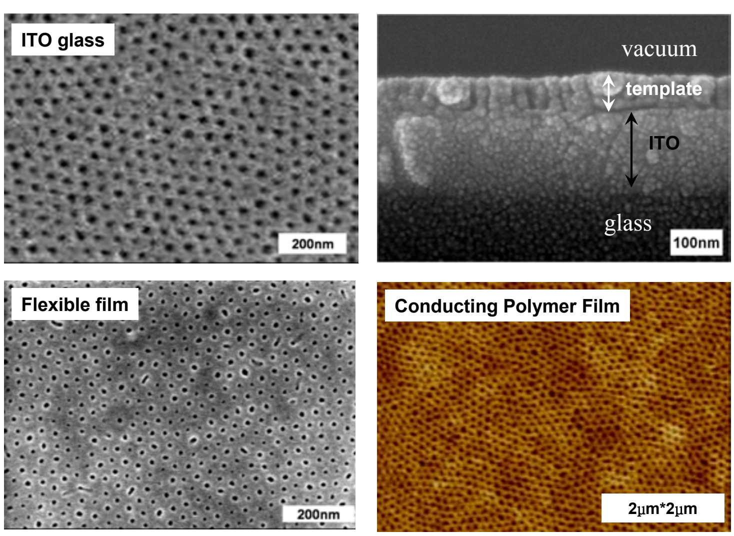
Lithium Perchlorate (Aldrich) $LiClO_4$

Propylene Carbonate (Acros)

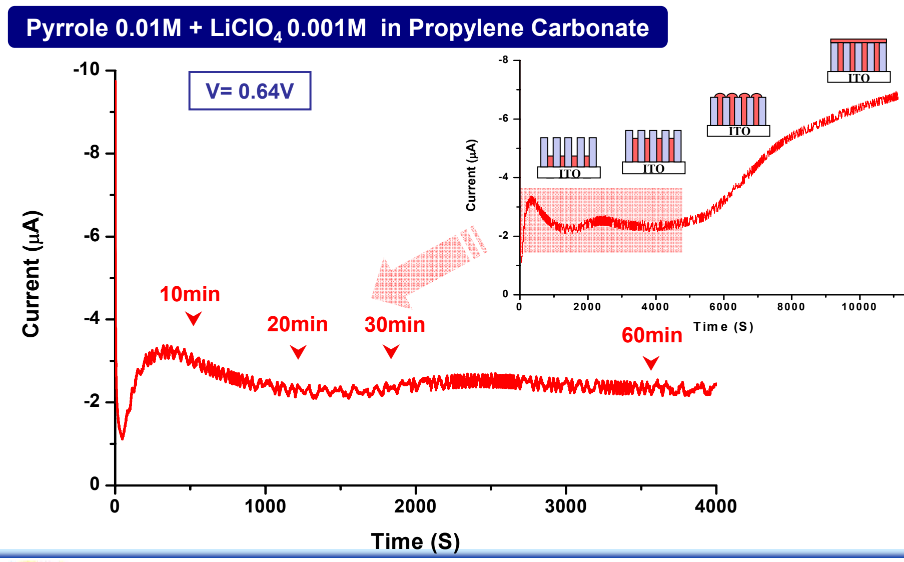
Instrument

- **Potentiostat** (Pro EChem System, AD Instrument)
- **Pt counter electrode**, **Non-aqueous Ag/Ag^+ reference electrode**
- **SEM with Focus Ion Beam, AFM**

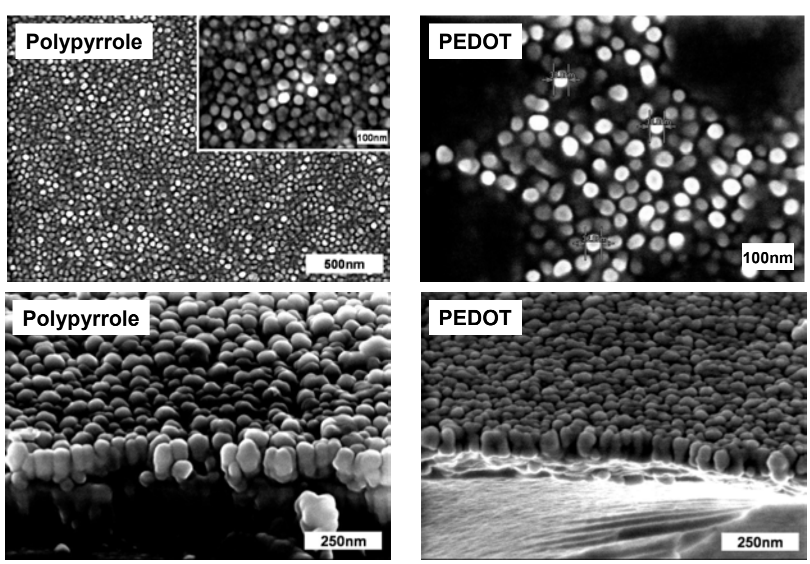
Perpendicularly Oriented Nanopores on Various Substrates



Electro-polymerization of Nanowires by Chromoamperogram



Surface and Cross-sectional Images of Conducting Polymer Nanowires



National Creative Research Initiative Center for Block Copolymer Self-Assembly

Summary

1. Vertically oriented Cylinders were possible for a film with more than 10 times of lattice spacing
2. Nanoporous Asymmetric Membranes made by Block Copolymer supported by MF Membrane showed High Flux (100 times more than PC Membrane) and High Selectivity for HRV 14 Viruses
3. Nanoporous Membrane can be used for the Separation and Purification of Protein and Viruses as well as Concentration of Biomaterials not easy to be Cultivated (Hepatitis C Virus)
4. Ultra-high Density Array of Nanowires of Conductive Polymers (Ppy and PEDOT) are successfully prepared by Electropolymerization inside Nanoholes

Block Copolymer Nanotemplates:
Promising Materials for Future Advanced Functional Materials

Acknowledgment

- National Creative Research Initiative Center for Block Copolymer Self-Assembly Supported by KOSEF
- D. Y. Ryu, U. Jeong, H. H. Lee (Former PhD students)
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- S. W. Oh, J. W. Yu (KIST) (Electropolymerization)
-T. P. Russell (U. Mass at Amherst) (Thin Film)
-D. H. Kim and W. Knoll (MPI) (Optical Waveguide Spectroscopy)

Membrane
Seung Yun Yang

PV Cells
Jeong In Lee
Jeong A Jang

National Creative Research Initiative Center for Block Copolymer Self-Assembly