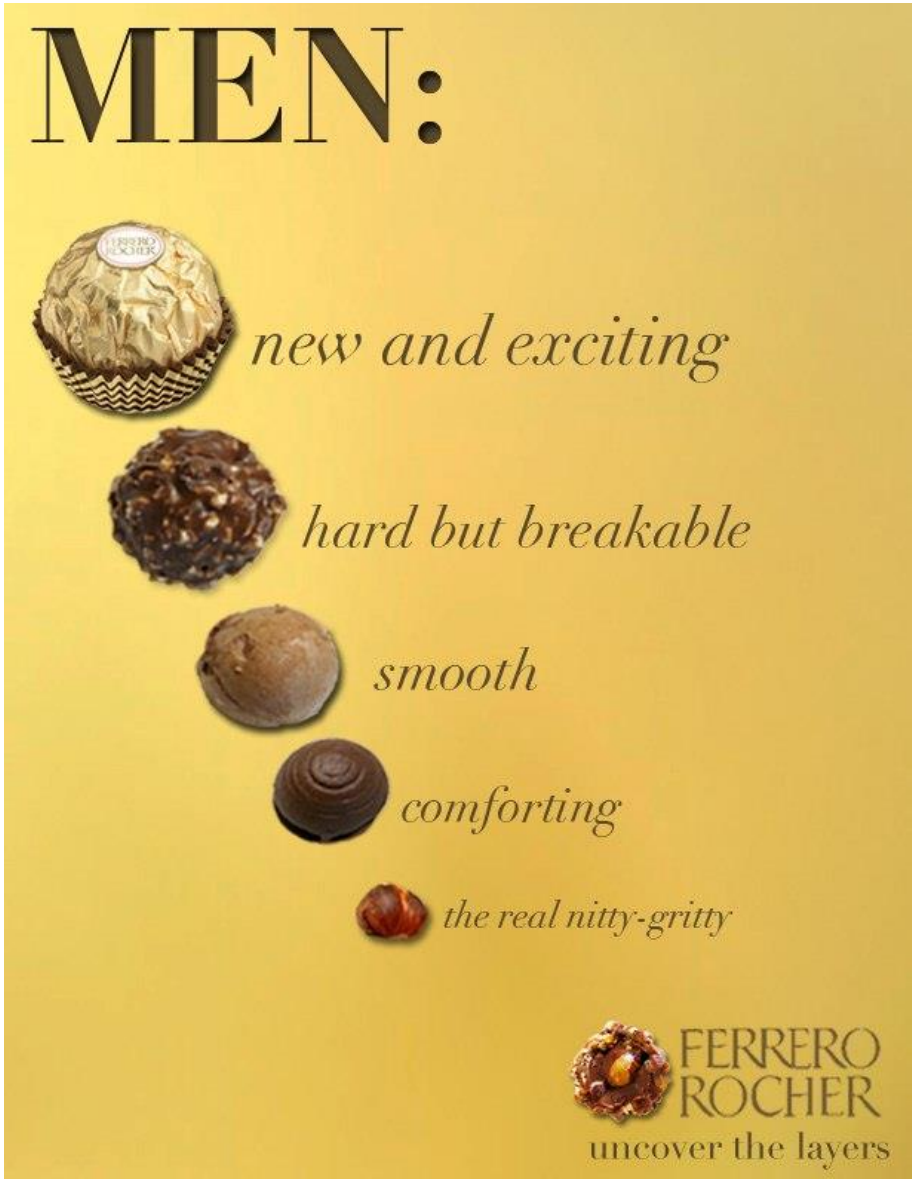
Layer-by-Layer (LBL) Self-Assembly



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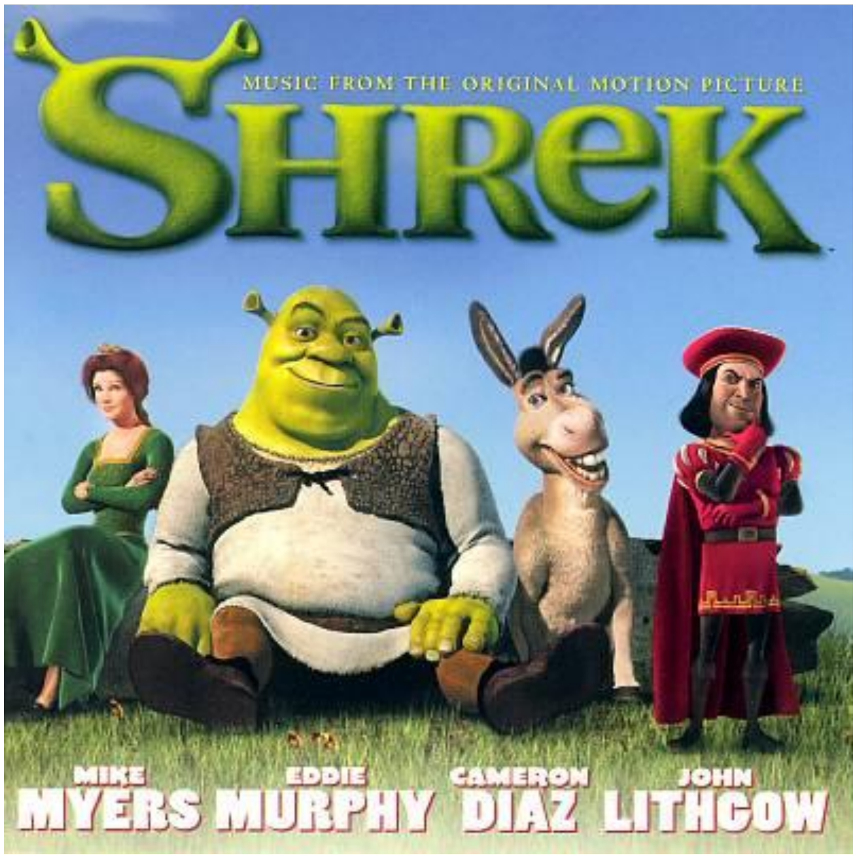
Layer-by-Layer (LBL) Self-Assembly



Sherk 2001

"No! Layers! Onions have layers! Ogres have Layers! Onions have Layers. You get it? We both have layers."

"Oh, you both have layers. Oh. You know, not everybody like onions."

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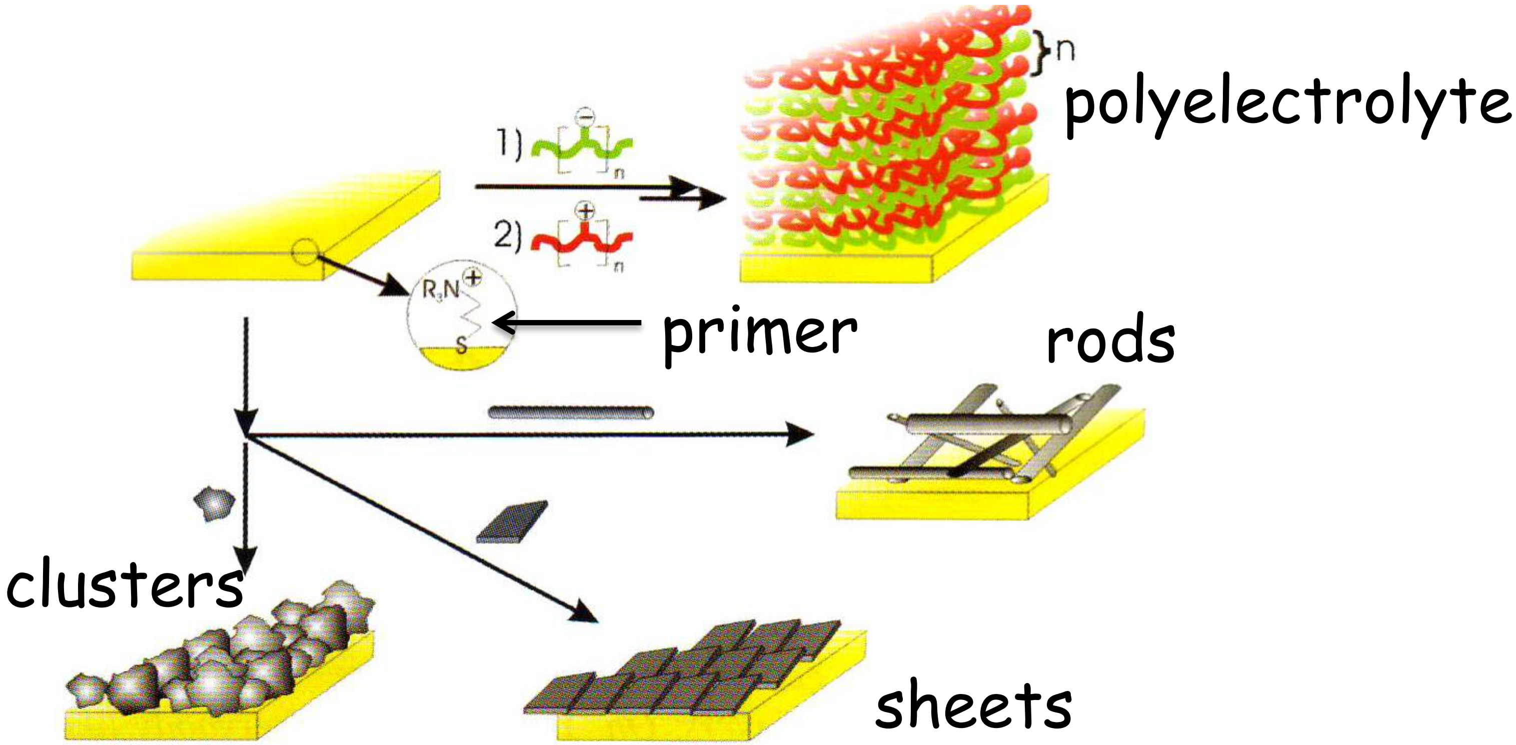
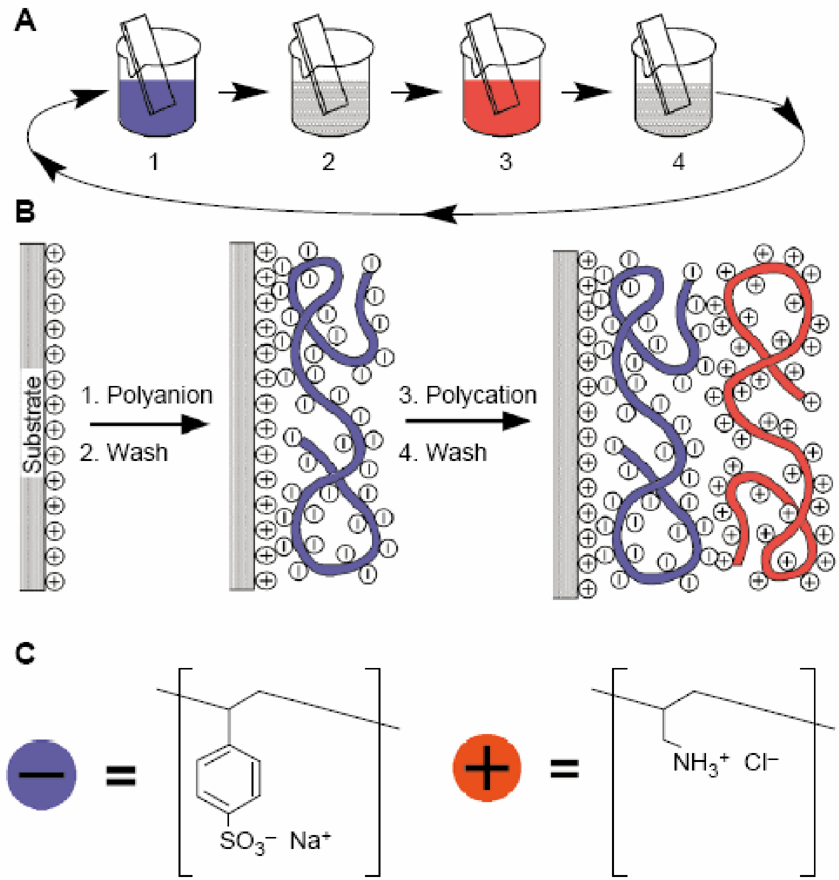
Layer-by-Layer (LBL) Self-Assembly



- If a layering process is repeated several times, the buildup can lead to three-dimensional materials.
- If we can control the vertical and lateral distribution of layers, we can control the shape, dimensions and compositions of 3D materials.

LBL Polyelectrolyte Assembly



Poly(styrene sulfonate) (PSS)

poly(allylamine hydrochloride) (PAH)

- Primer layer serves to impart a surface with a charge.
- The charged surface is able to electrostatically bind a water-soluble anionic polyeletrolyte, which is held tightly by multiple electrostatic interactions.
- A molecule bearing a few charges on it would only be weakly bound.
- Polyelectrolytes are macromolecules: after neutralize charges on surface, still a few charged repeat units dangling above.

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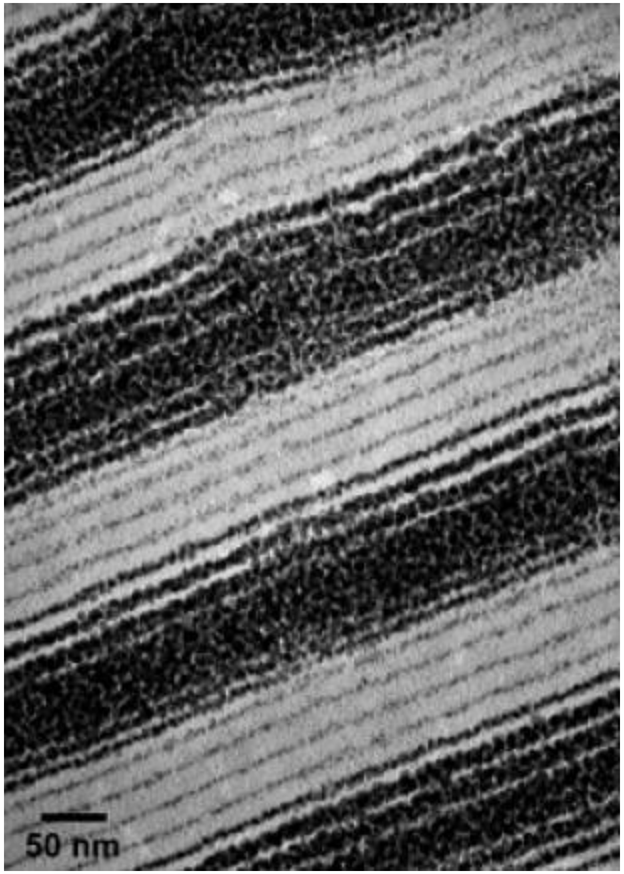
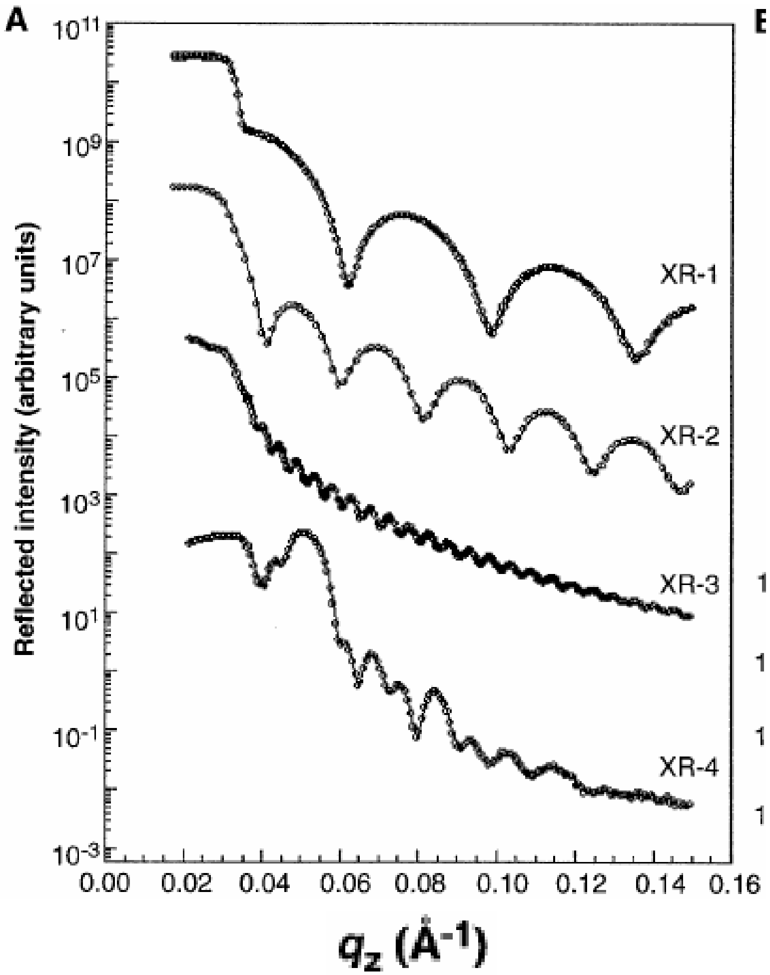
Characterization of Layers

Direct Imaging by TEM



Dark lines - Ag

X-Ray Reflectivity



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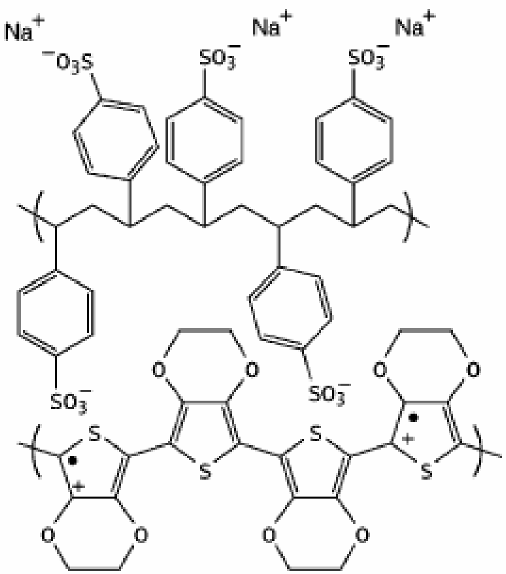
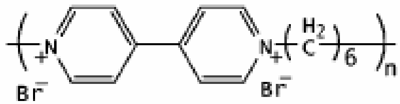
LBL Smart Windows

Electrochromic System



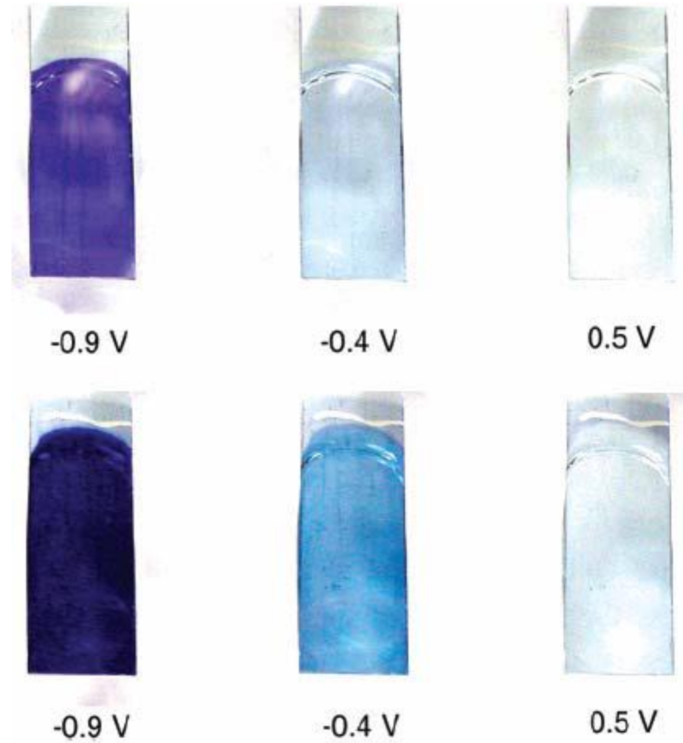
PEDOT:SPS



PXV

40 Bilayers

60 Bilayers

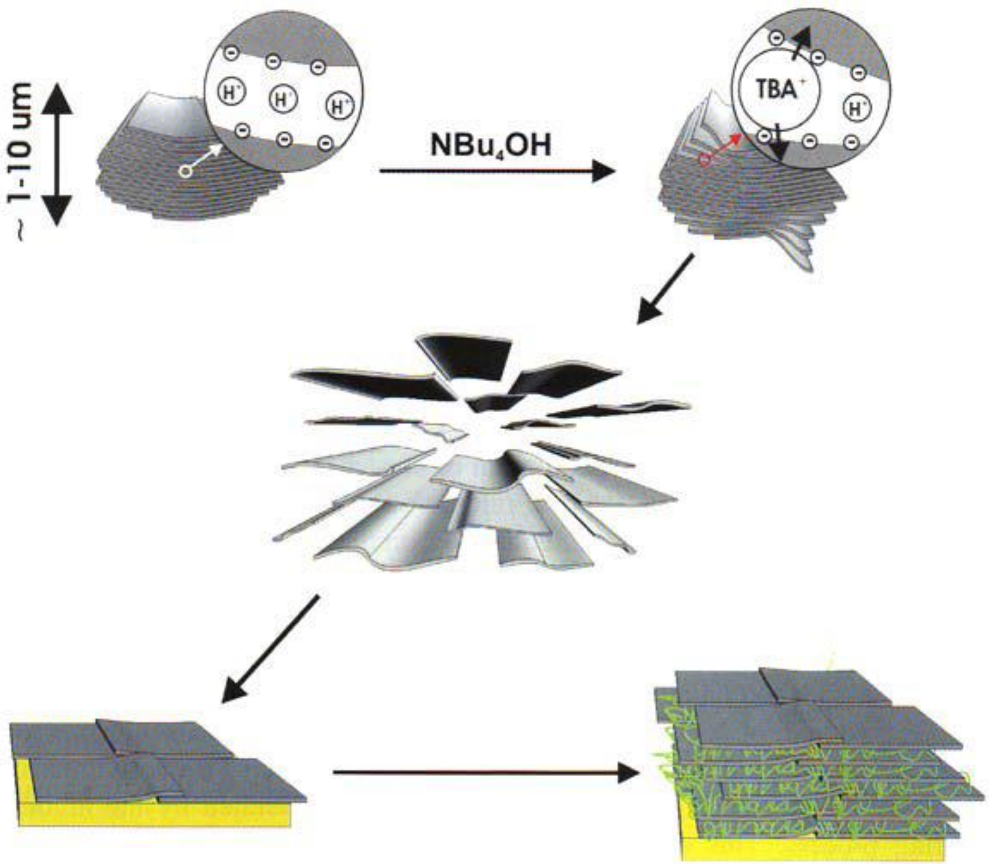


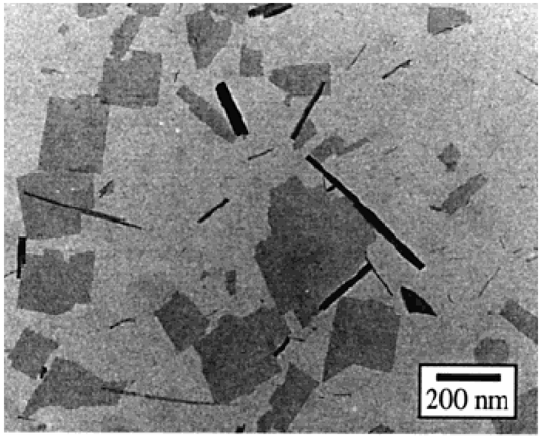
- Polyelectrolyte films can indeed be used as electrochromics.
- At a negative potential, colorless PXV undergoes a reduction to its deep-blue clolored radical cation, and the PEDOT:PSS also becomes colored due to an undoping of the conductive state

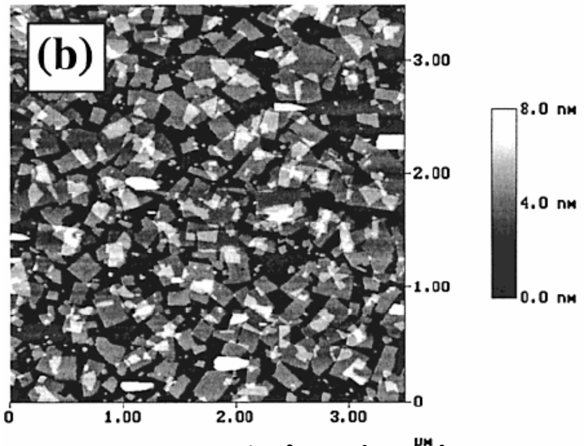
(*Chem. Mater.* **15**, 1575, 2003)

Polyelectrolyte-Colloid Multilayers

Exfoliation of Anionic Layered Materials $TBA_xH_{2-x}CaNaTa_3O_{10}$







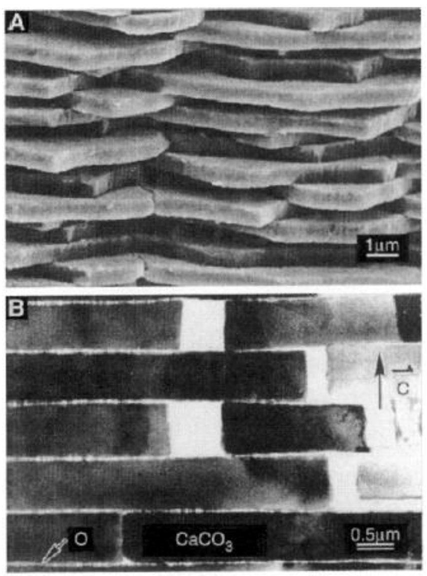
(graphite, perovskites, clay, etc.)

LBL Assembled Sheets

(Chem. Mater. **12**, 3427, 2000)

Nanostructured Artificial Nacre

Natural Nacre



LBL deposition of clay and polyelectrolyte for artificial nacre

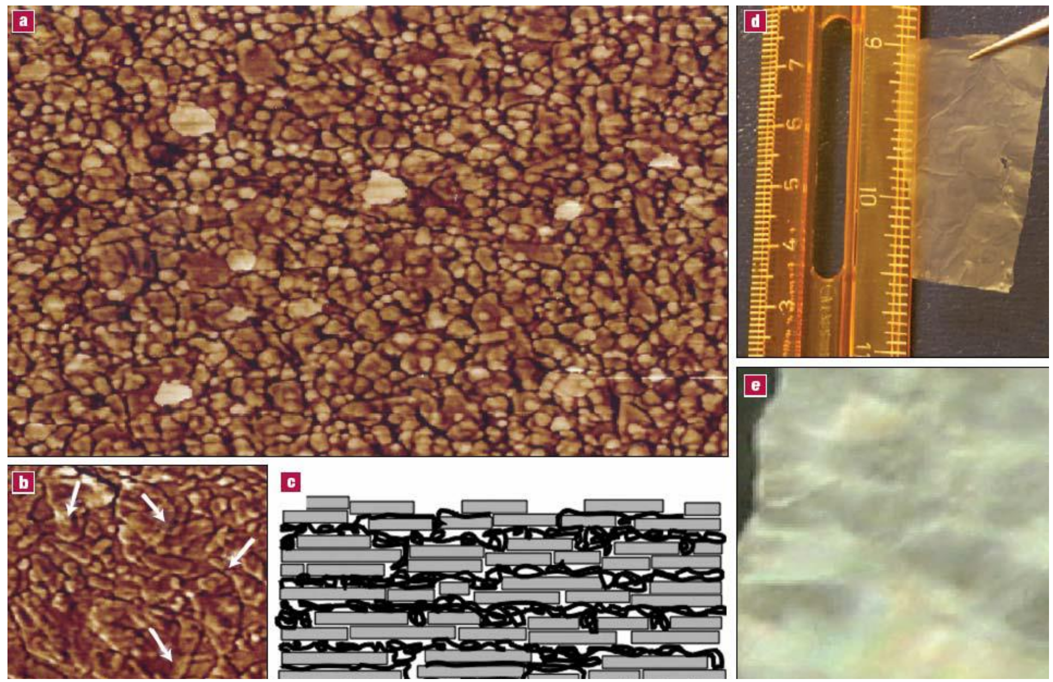


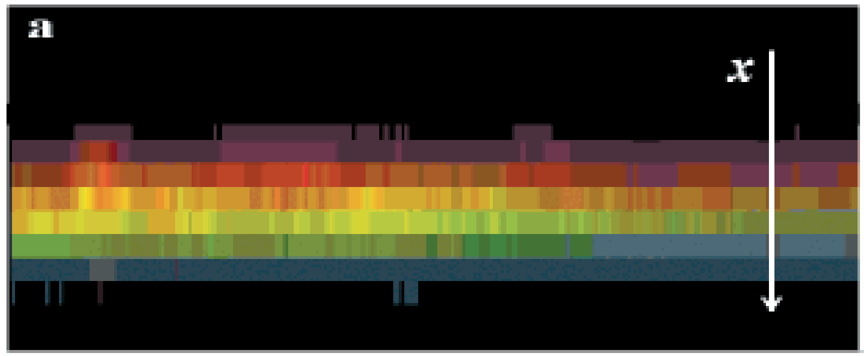
Table 1 Mechanical properties of $(P/C)_n$ films with different n

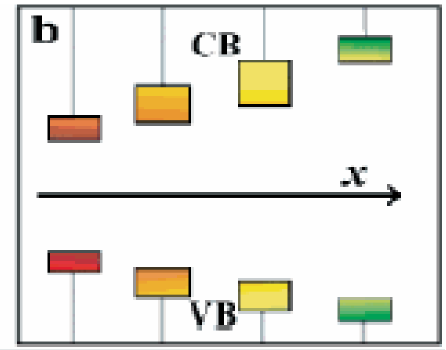
Number of deposition cycles, n	Thickness from TEM (μm)	Ultimate stress, σ_u (Mpa)	Ultimate strain, ε_u	Young modulus, E (GPa)
50	1.2 ± 0.05	95 ± 12	0.068 ± 0.005	9 ± 2
100	2.4 ± 0.05	106 ± 8	0.084 ± 0.007	10 ± 2
200	4.9 ± 0.06	109 ± 8	0.10 ± 0.005	13 ± 2

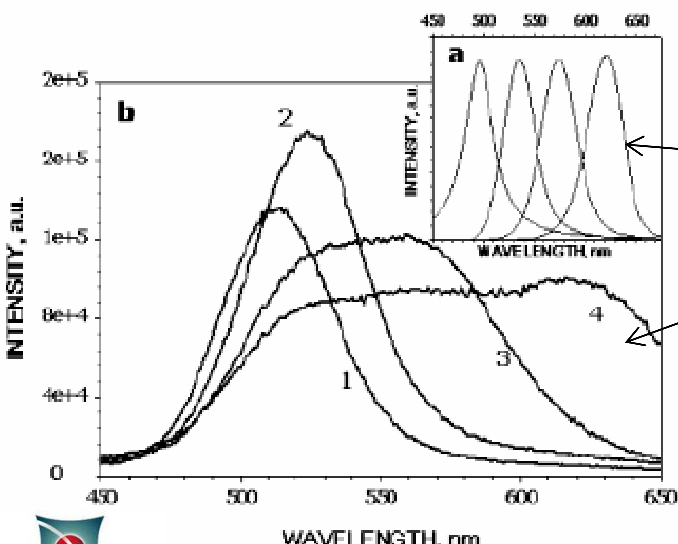
(*Nature Mater.* **2**, 413, 2003)

Graded Composition LBL Films: Nanorainbow

CdTe nanocrystals show size-dependent band gap (color)

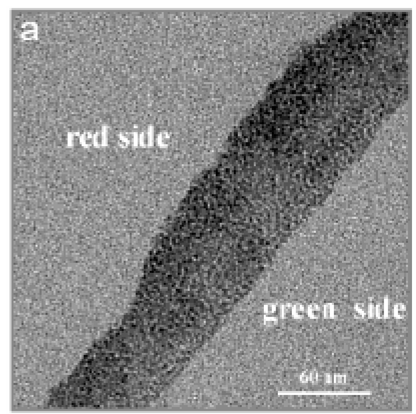


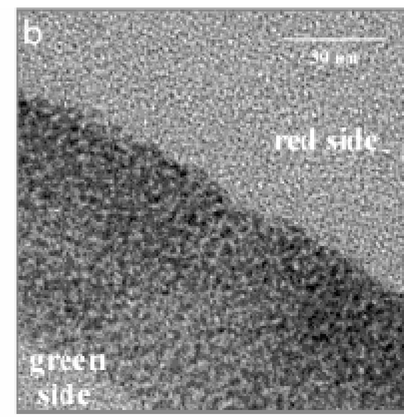




NPs

LBL Films

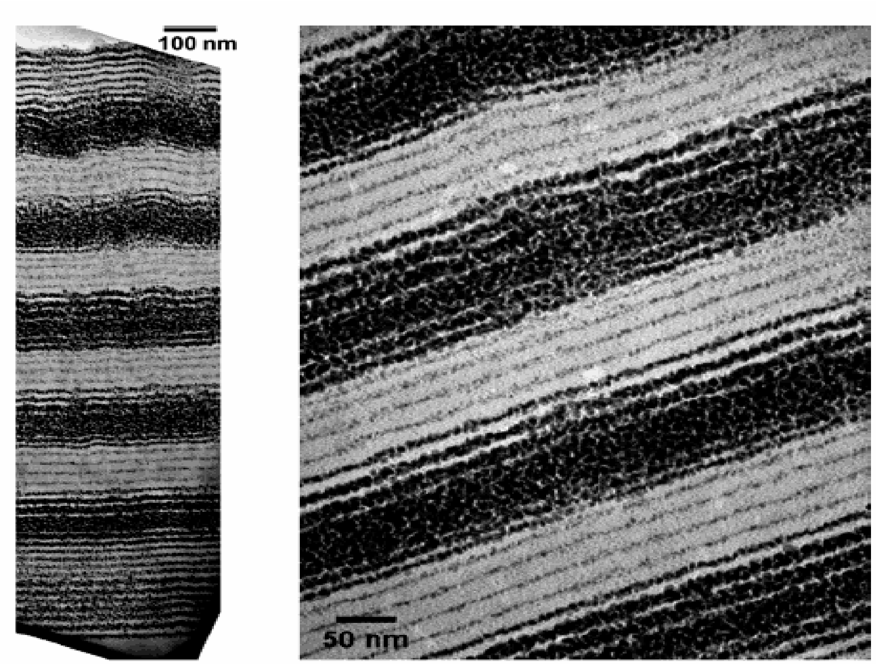


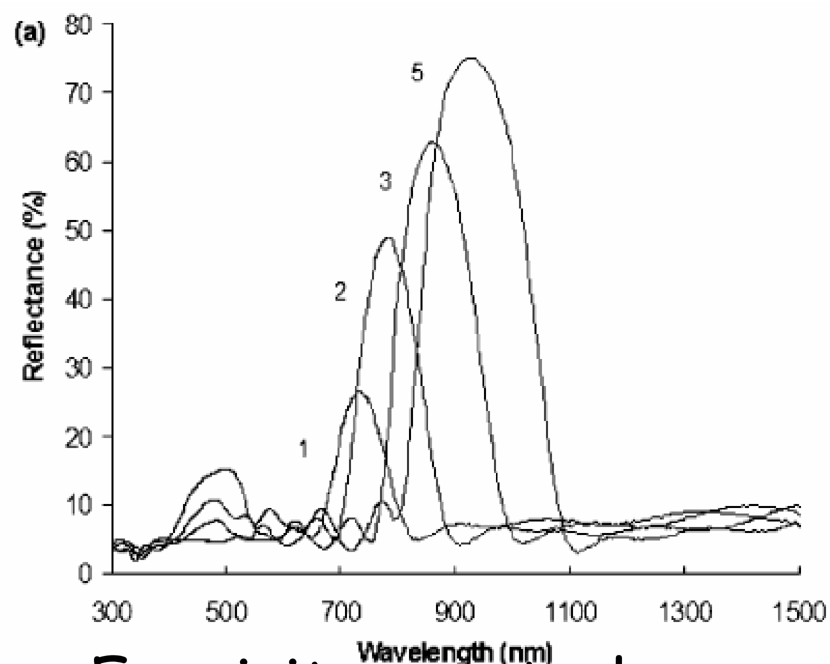


LBL of anionic thioglycolic acid capped CdTe nanoparticles and cationic poly(diallydimethylammonium chloride).

(*JACS* **123**, 7738, 2001)

Molecularly Assembled Dielectric Mirror

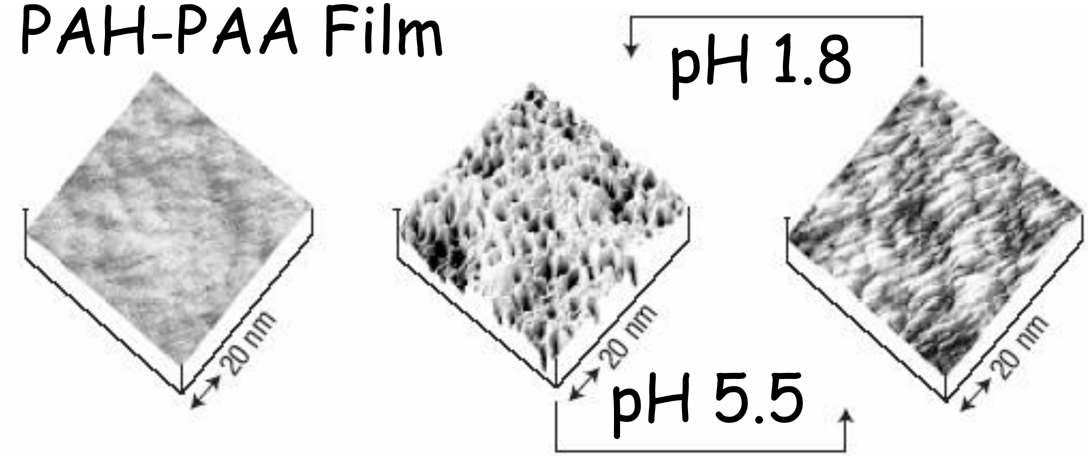


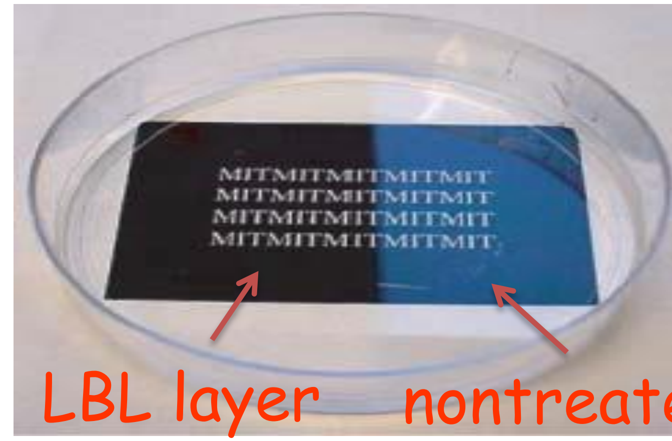


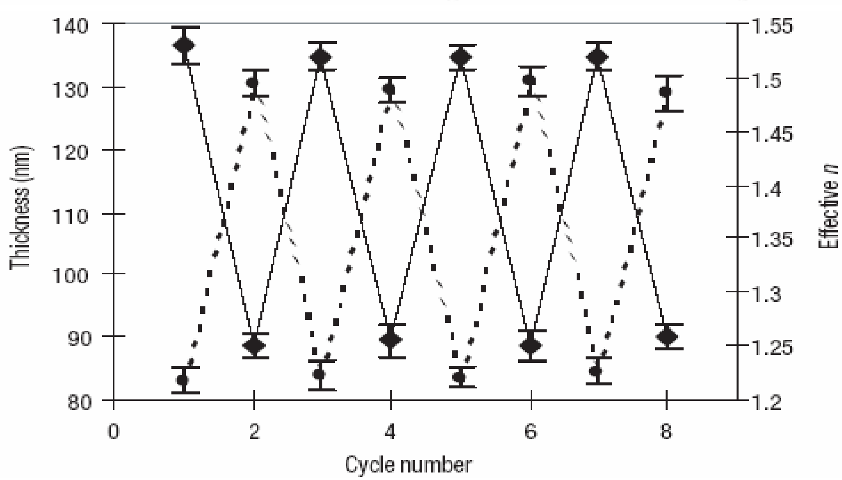
- Ag gradient index formed by cationic exchange of Ag ions with protons in LBL assembled PAH-PAA multilayers followed by reduction and preferential aggregation of Ag particles.
- Exquisite control over the individual layers in the LBL process results in a considerable command over optical properties.

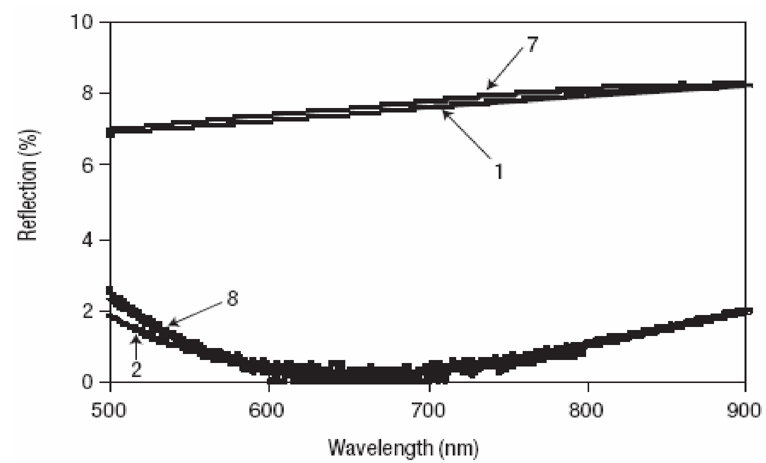
LBL Assembled Anti-reflection Coatings on Flexible Substrates

PAH-PAA Film









Phase-separated LBL polyelectrolyte multilayer films undergo a reversible pH-induced swelling transition.

(*Nature Mater.* **1**, 59, 2002)

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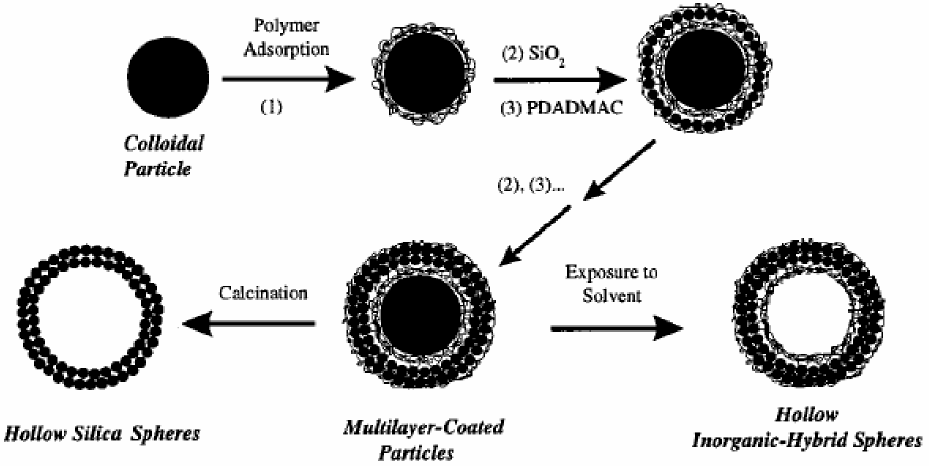
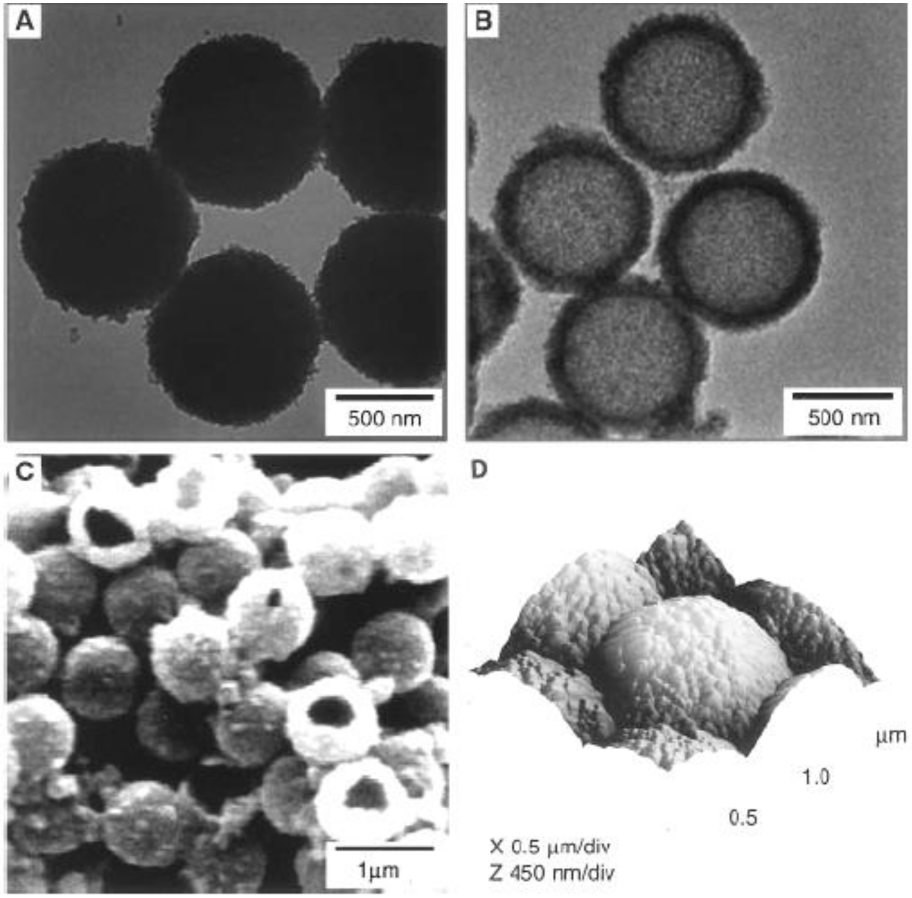
LBL on Colloidal Particles





SiO_2/PDADMAC Hollow Spheres

- LBL of silica nanoparticles and polyelectrolyte, followed by removal of polystyrene sphere template, results in hollow spheres that have important applications as drug delivery media.

(*Science* **282**, 1111, 1998)

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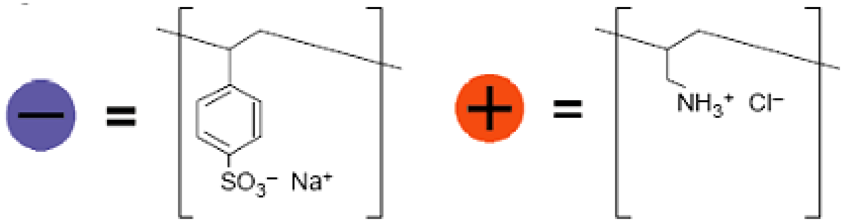
Applications for LBL Self-Assembly

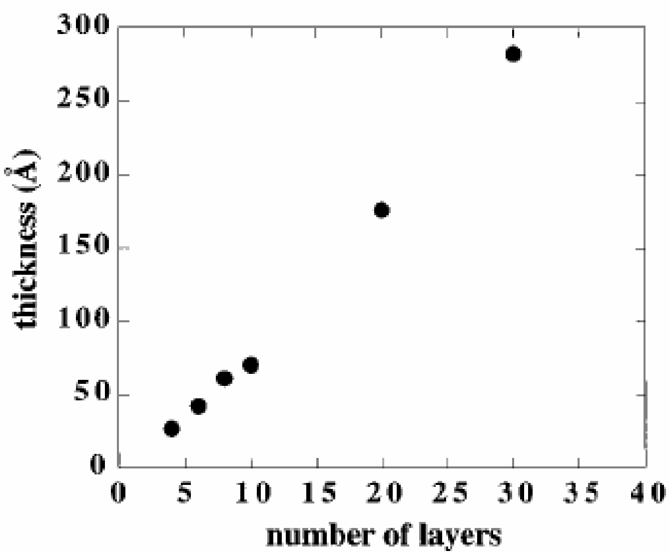
We focus on three key applications:

- Perm-Selective Thin Films and Sensors
- Solid-State Electrolytes
- Crystal Engineering of Oriented Crystal Arrays

LBL Perm-Selective Membrane



PSS PAH



PAH/PSS multilayer on PMP-COOH film

(*Macromolecules* **30**, 1752, 1997)

Gas Permeability of LBL Membranes

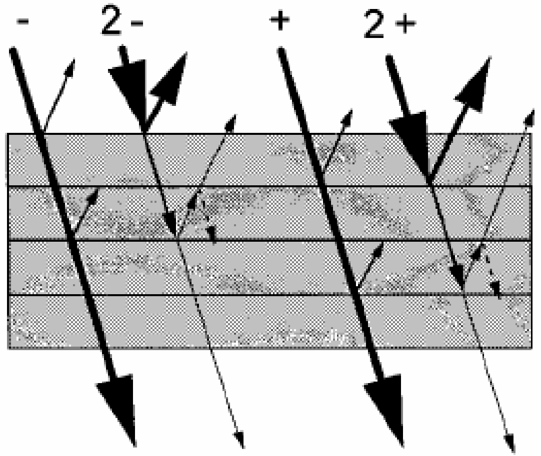
sample	$P(N_2)^a$	$P(O_2)^a$	$P(H_2)^a$
PMP	1.3	5.4	22.0
PMP−COOH	1.3	4.1	17.5
PMP−COOH/PAH/PSS			
10 layers	0.95	4.2	16.8
20 layers	0.35	2.1	16.4
50 layers	0.13	1.0	13.3
100 layers	0.13	0.97	13.3
200 layers	0.08	1.2	9.7

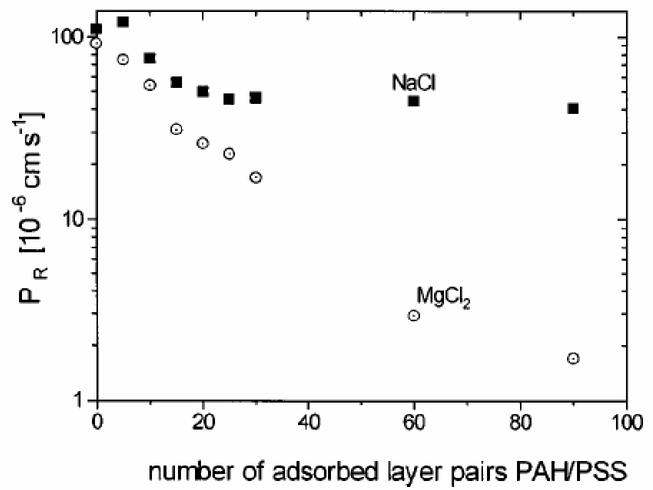
[a] 10^{-9} cm^3 (STP) cm/cm^2 s cm(Hg).

- High charge densities and strong ionic interactions results in close packing of polymer chains that are immobilized by ionic cross-links between charged functionalities in repeat units.
- High restrictions in segmental motion within the layers leads to selective gas permeability.

Selective Ion Transport through LBL Multilayers

Rejection of multivalent ions





no. of adsorbed layers	P_R (NaCl) $[10^{-6}$ cm s$^{-1}]$	P_R ($MgCl_2$) $[10^{-6}$ cm s$^{-1}]$	α (Na^+/Mg^{2+})	P_R (Na_2SO_4) $[10^{-6}$ cm s$^{-1}]$	α (Cl^-/SO_4^{2-})
		(a) with Addition of NaCl			
5	62.6	2.0	31.3	3.7	16.9
10	39.2	1.1	35.6	1.5	26.1
60	22.5	0.2	112.5	0.5	45.0
		(b) without Addition of NaCl			
5	121.7	74.7	1.6	*a*	*a*
10	75.6	54.0	1.4	*a*	*a*
60	44.4	2.9	15.1	4.5	9.9

[a] Not determined.

- The presence of fixed charges at the surface of the multilayers results in Donnan exclusion of multivalent ions.

(*Langmuir* **16**, 287, 2000)

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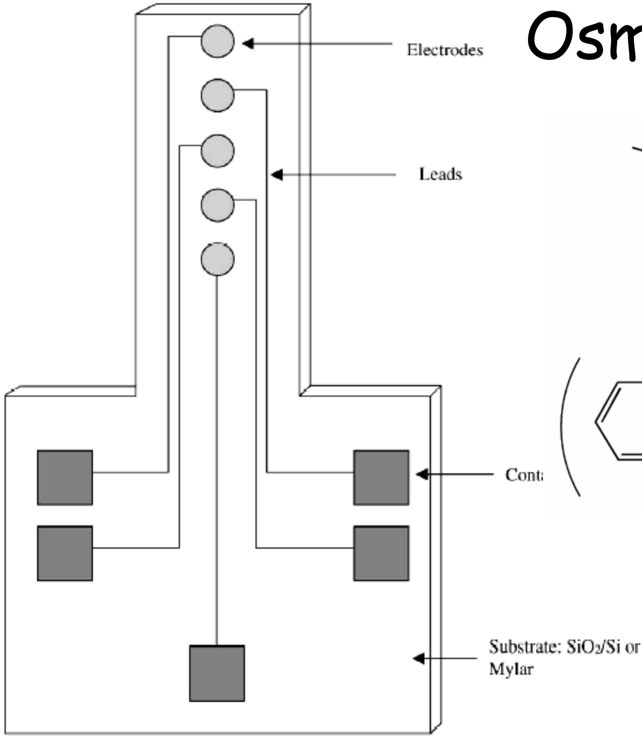
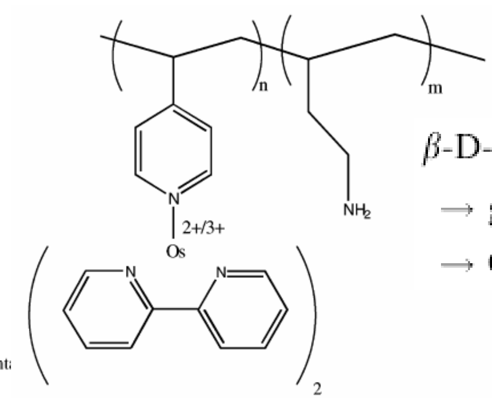
LBL Thin Film Bio-sensors

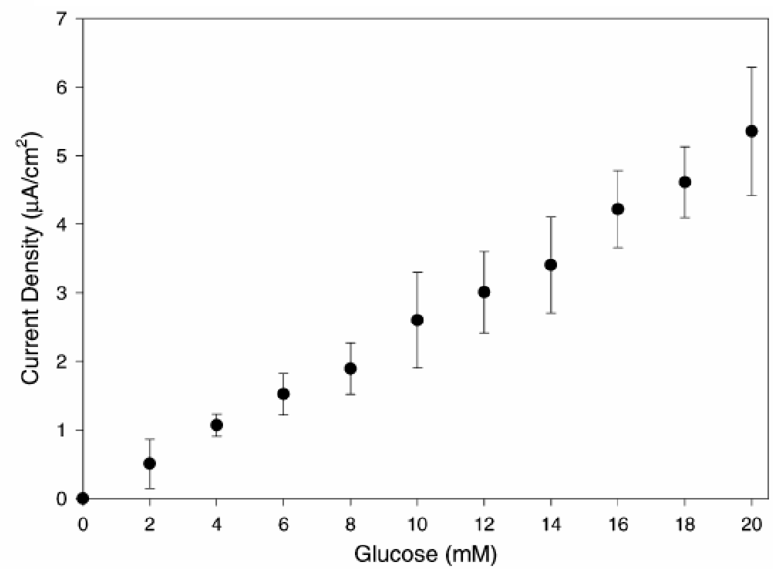


Osmium Polymer



Redox Reaction

$$\beta\text{-D-glucose} + \text{GOX(FAD)} \rightarrow \text{gluconolactone} + \text{GOX(FADH}_2\text{)} \quad \text{GOX(FADH}_2\text{)} + 2\text{M}^{2+} \rightarrow \text{GOX(FAD)} + 2\text{M}^{+}$$



LBL assembly using a polycationic osmium redox polymer and a polyanionic enzyme, GOX on Au

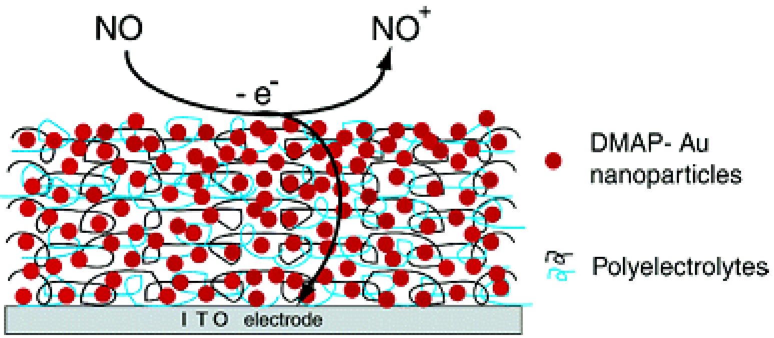
National ChungHsing University

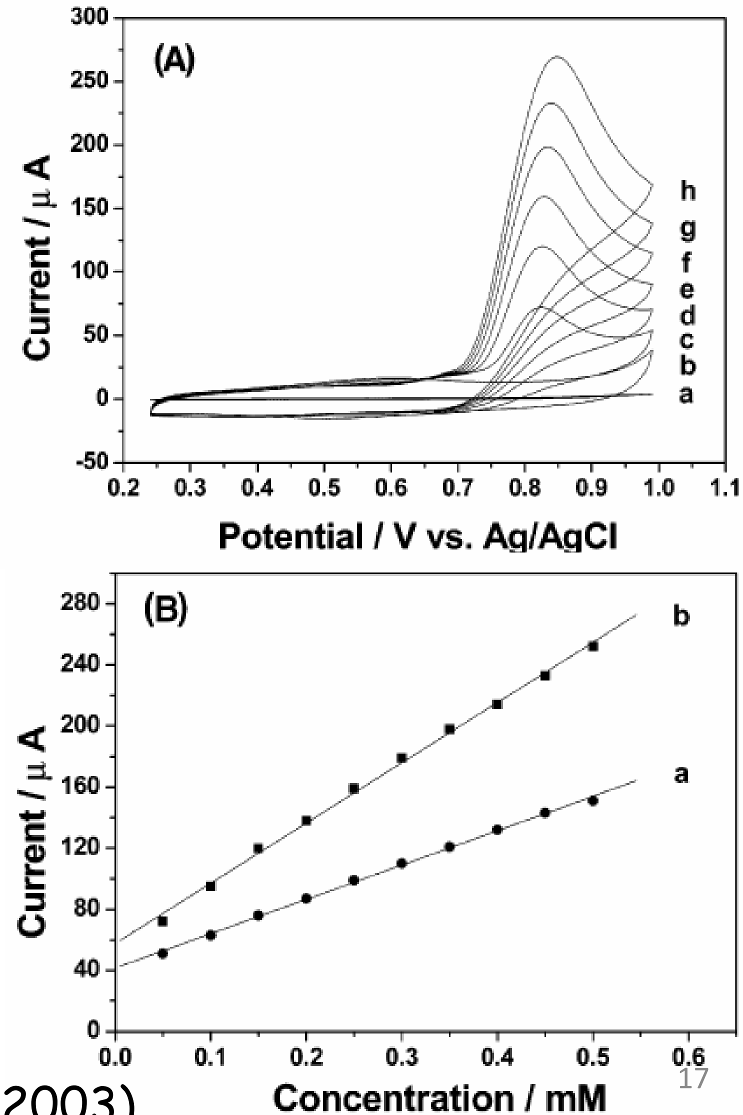
(*Sens. Actuators* B **81**, 359, 2002)

Electrochemical Sensors Based on LBL Assembled Nanoparticle Films

Release of NO from $NaNO_2$:

$$3HONO \rightarrow H^+ + NO_3^- + 2NO + H_2O$$





The presence of gold nanoparticles in the PE multilayers could significantly improve the electron-transfer characteristics of the films, which show high electrocatalytic activity to the oxidation of nitric oxide (NO).

(*Nano Lett.* **3**, 1203, 2003)

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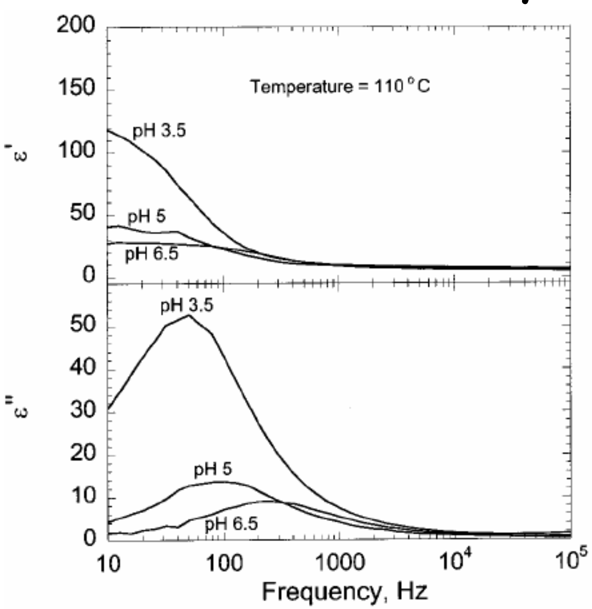
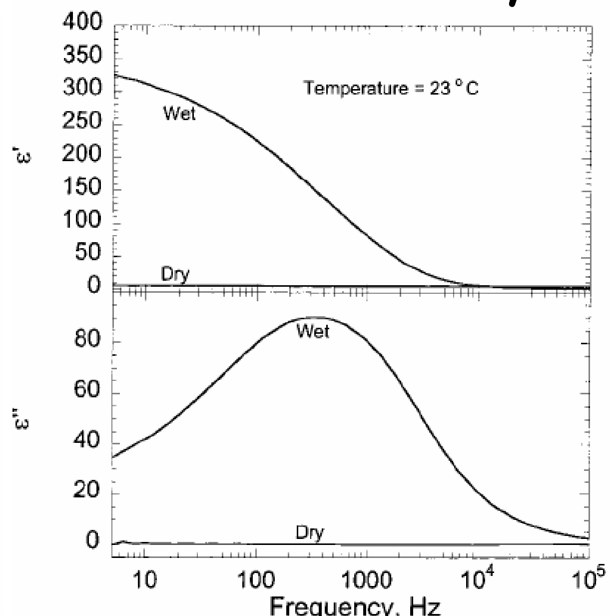
LBL Solid-State Electrolytes - Ionic Conductivities

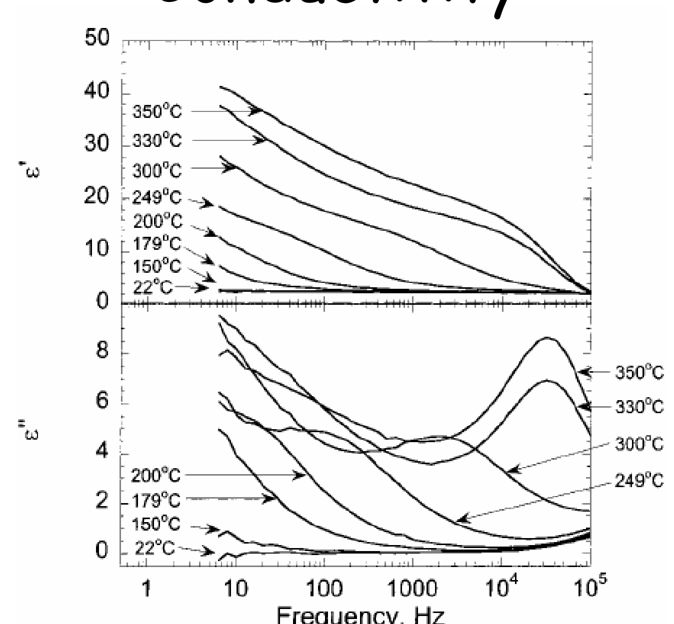
Dipping Solution pH on Conductivity



Humidity on Conductivity



Temperature on Conductivity



- Changes in the dielectric characteristics of PAA/PAH films with changes in temp., moisture content, and solution pH.
- If ionic conductivity increased, LBL films will have applications for OLEDs and fuel cells.

(*Langmuir* **17**, 7865, 2001)

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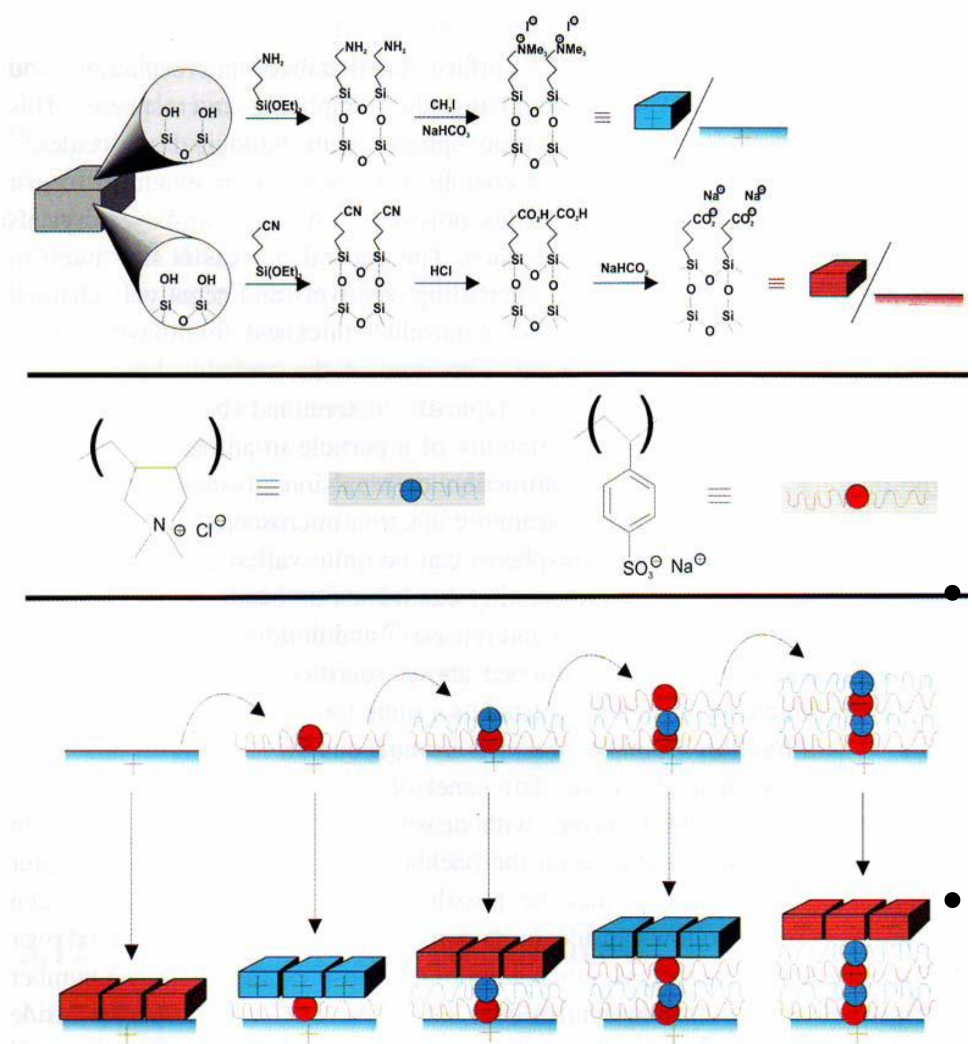
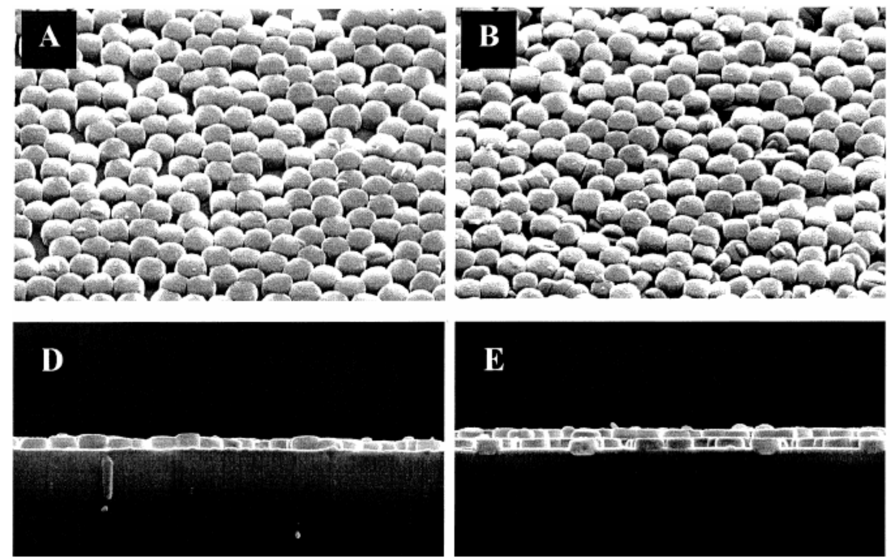
Crystal Engineering - Oriented Zeolite Film

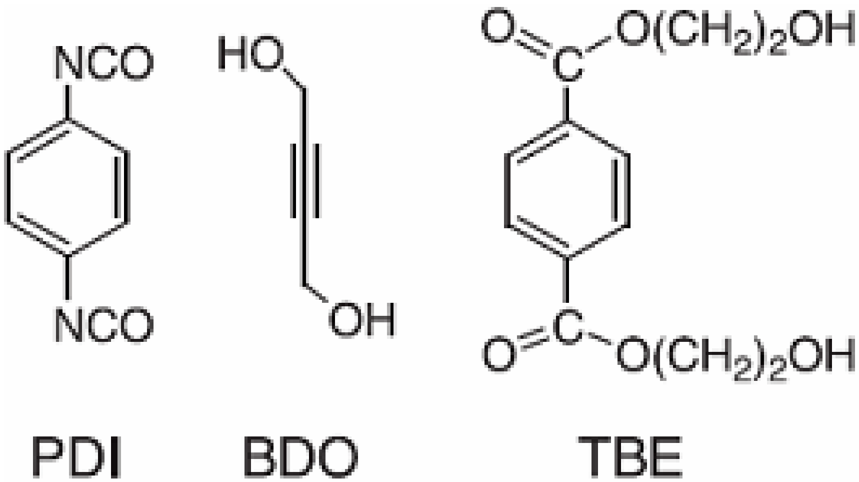


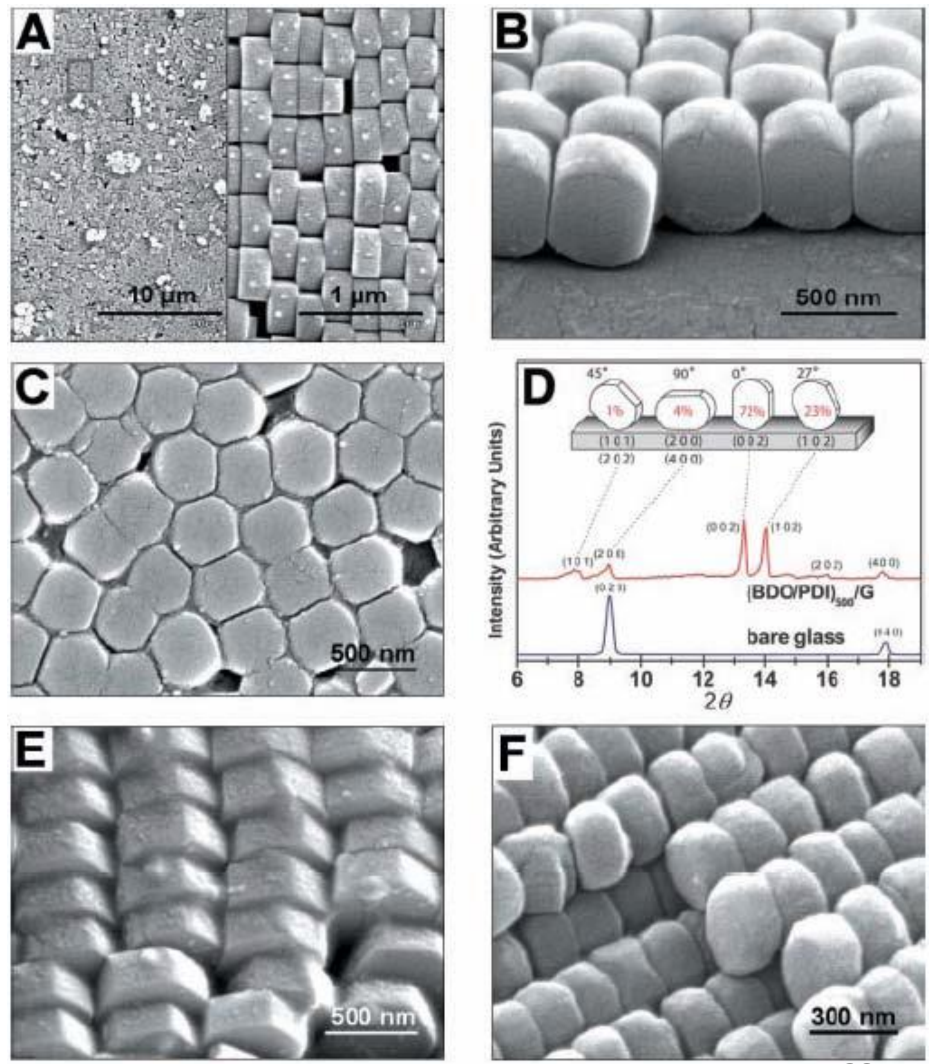
(*J. Am. Chem. Soc.* **123**, 9769, 2001)



- Zeolites are important materials used for catalysis, separation, detergents and waster remediation.
- Zeolites are required as membranes or thin films for many of these applications.

Zeolite-Ordered Multicrystal Arrays

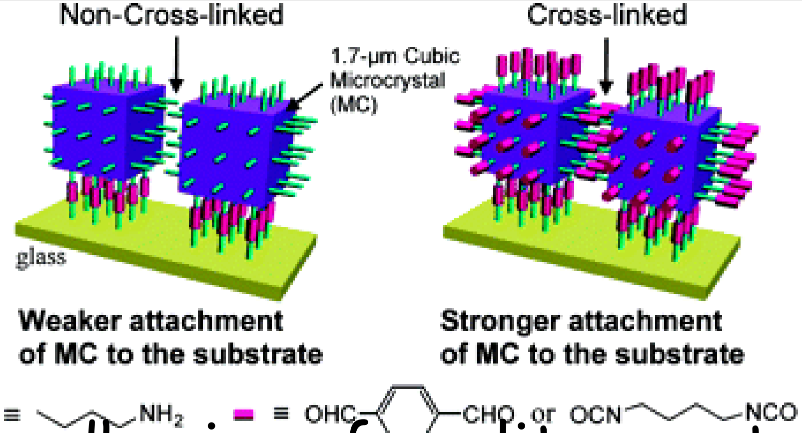


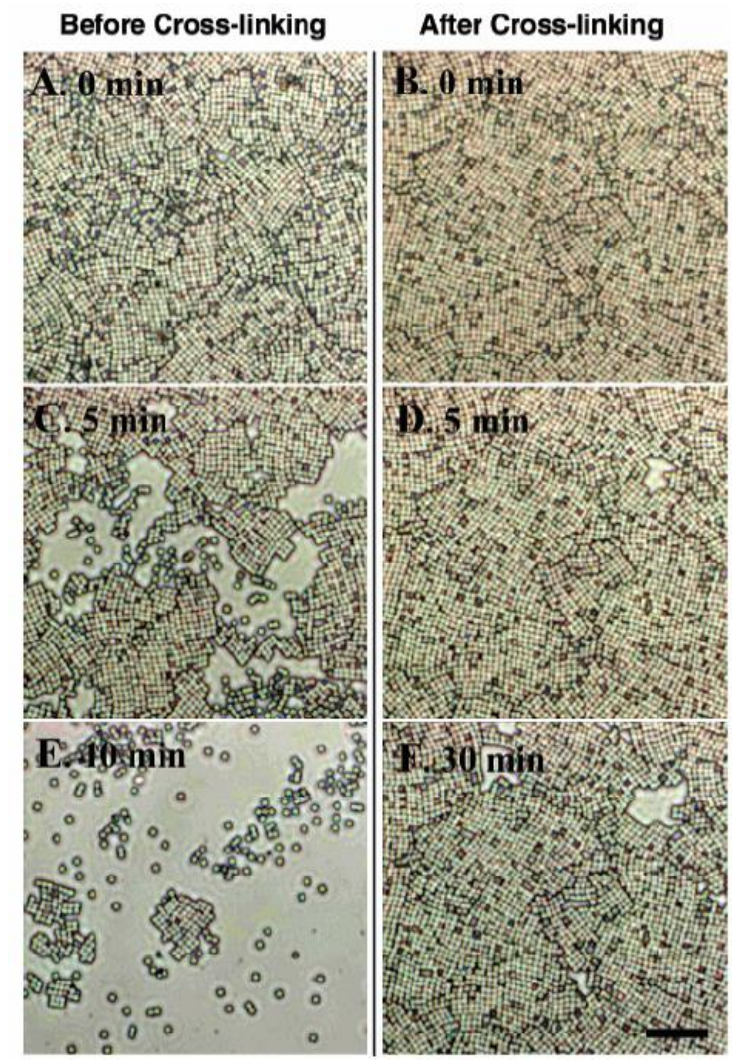


- Oriented polyurethane (PU) chains form by LBL assembly of PDI and BDO or TBE.
- PU chains as templates to achieve vectorial control of the nucleation and growth of zeolites.

(*Science* **301**, 818, 2003)

Crosslinked Crystal Arrays



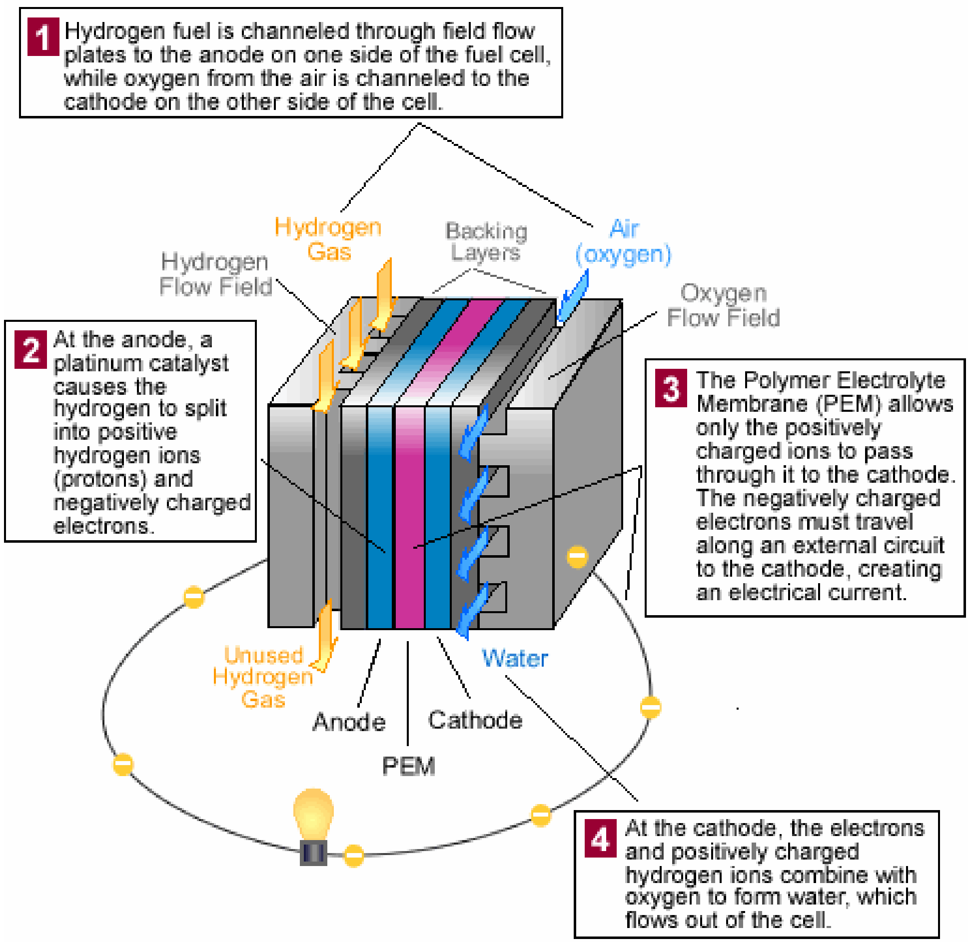


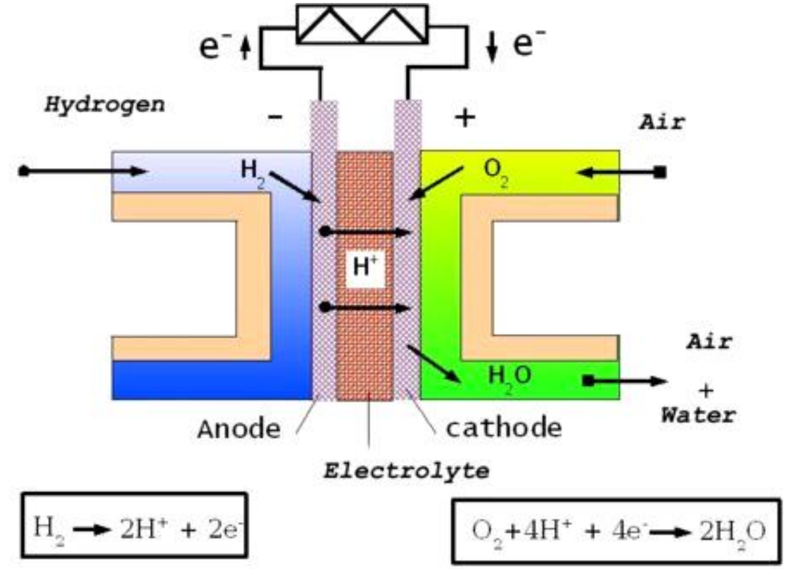
Under Ultrasonication

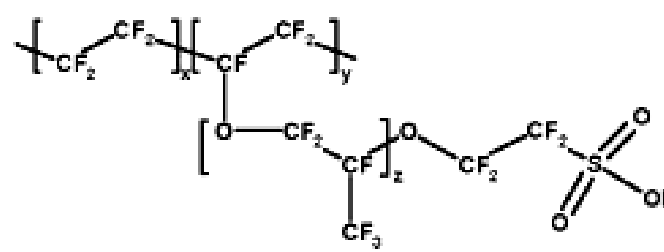
- The adhesion of zeolite crystals to the substrate is week due to small area to large mass ratio.
- Chemically crosslinking the crystals through imine or urethane linkage.
- The functionalization is surface specific as the molecule is too large to enter the eight-ring pore.

(*J. Am. Chem. Soc.* **126**, 1934, 2004)

PEM Fuel Cell – An important Application Area for LBL Polyelectrolyte Multilayers







PEM Materials - Nafion

- Perm-selectivity and relatively high ionic conductivity of LBL multilayer films are of great interest for fuel cell applications