Exfoliated Oxide Nanosheets

–New Solution to Tailored Nanoelectronics–

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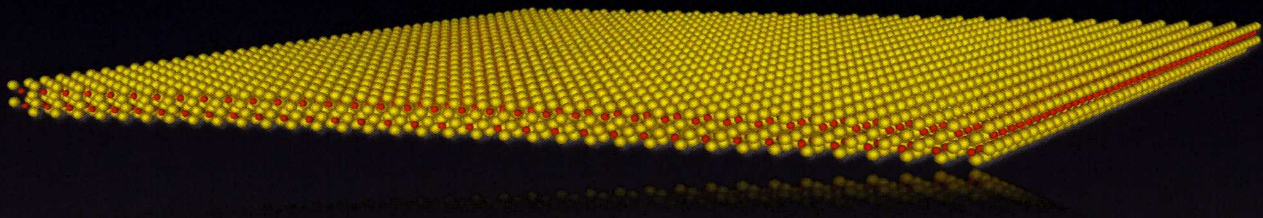
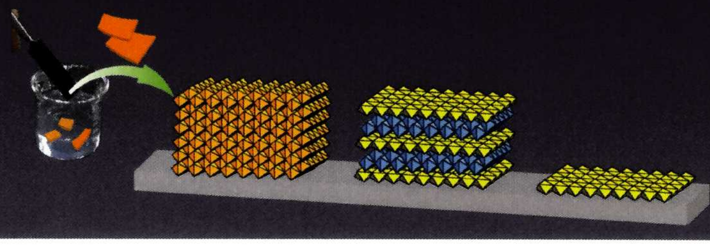


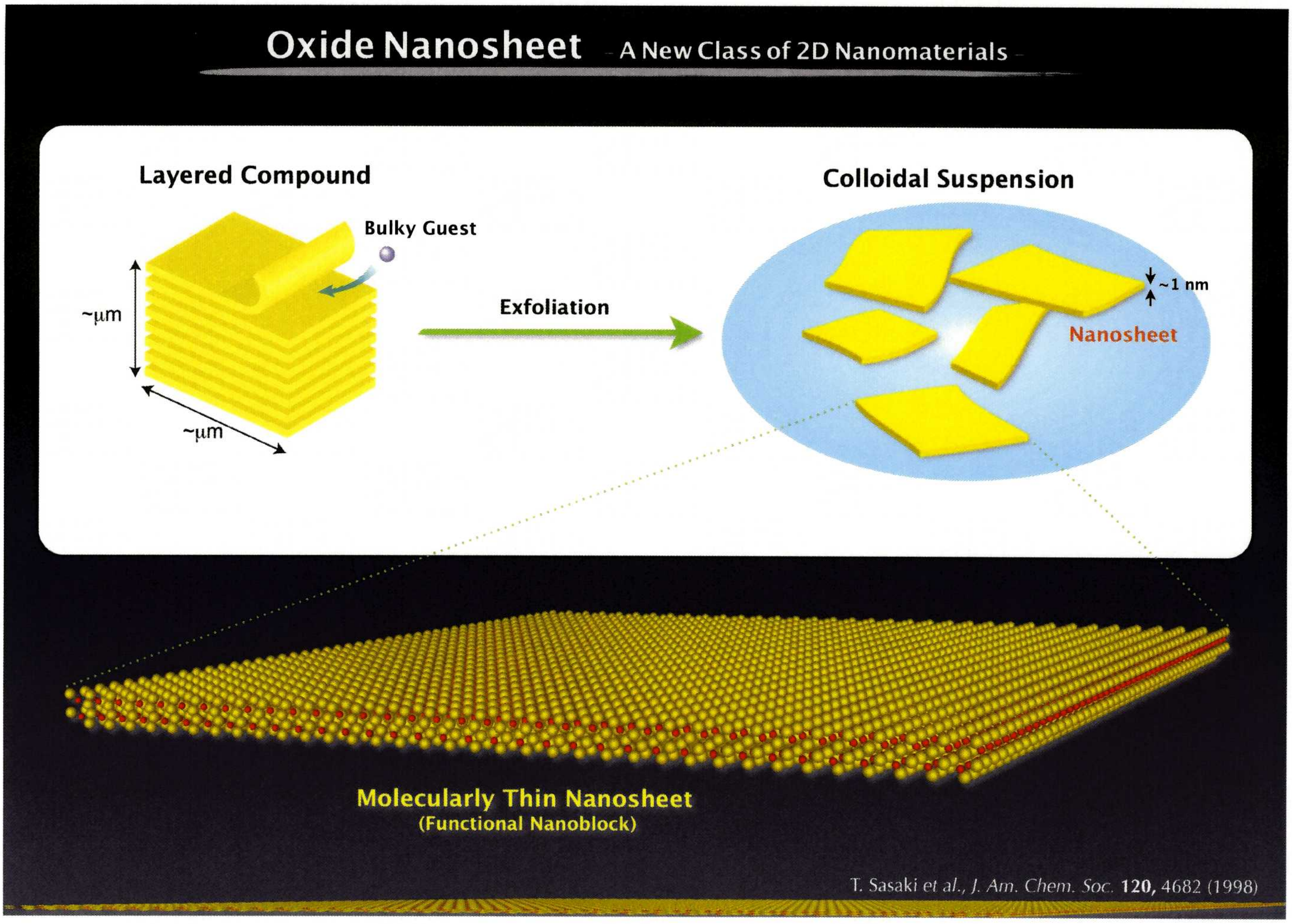


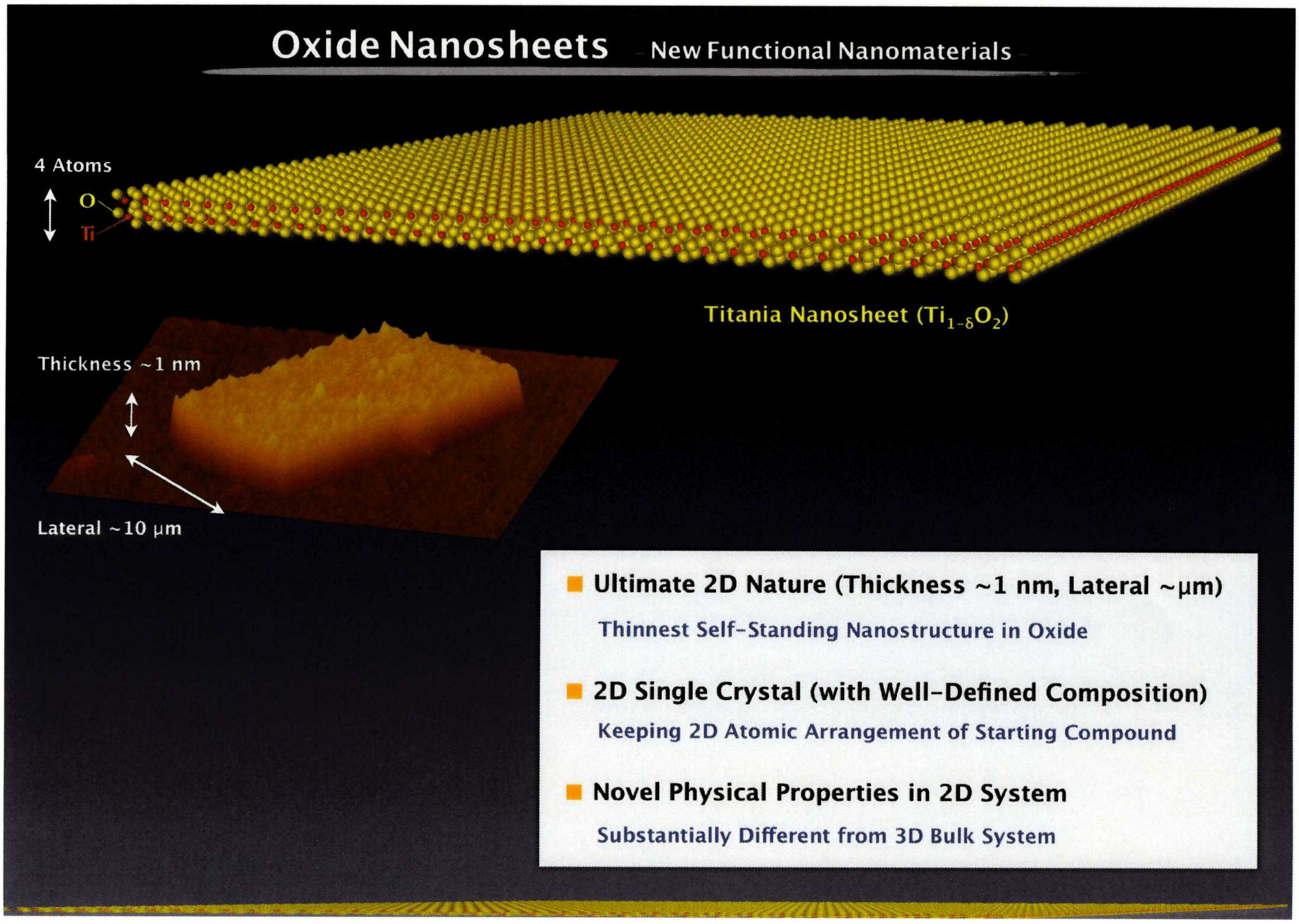
Outline

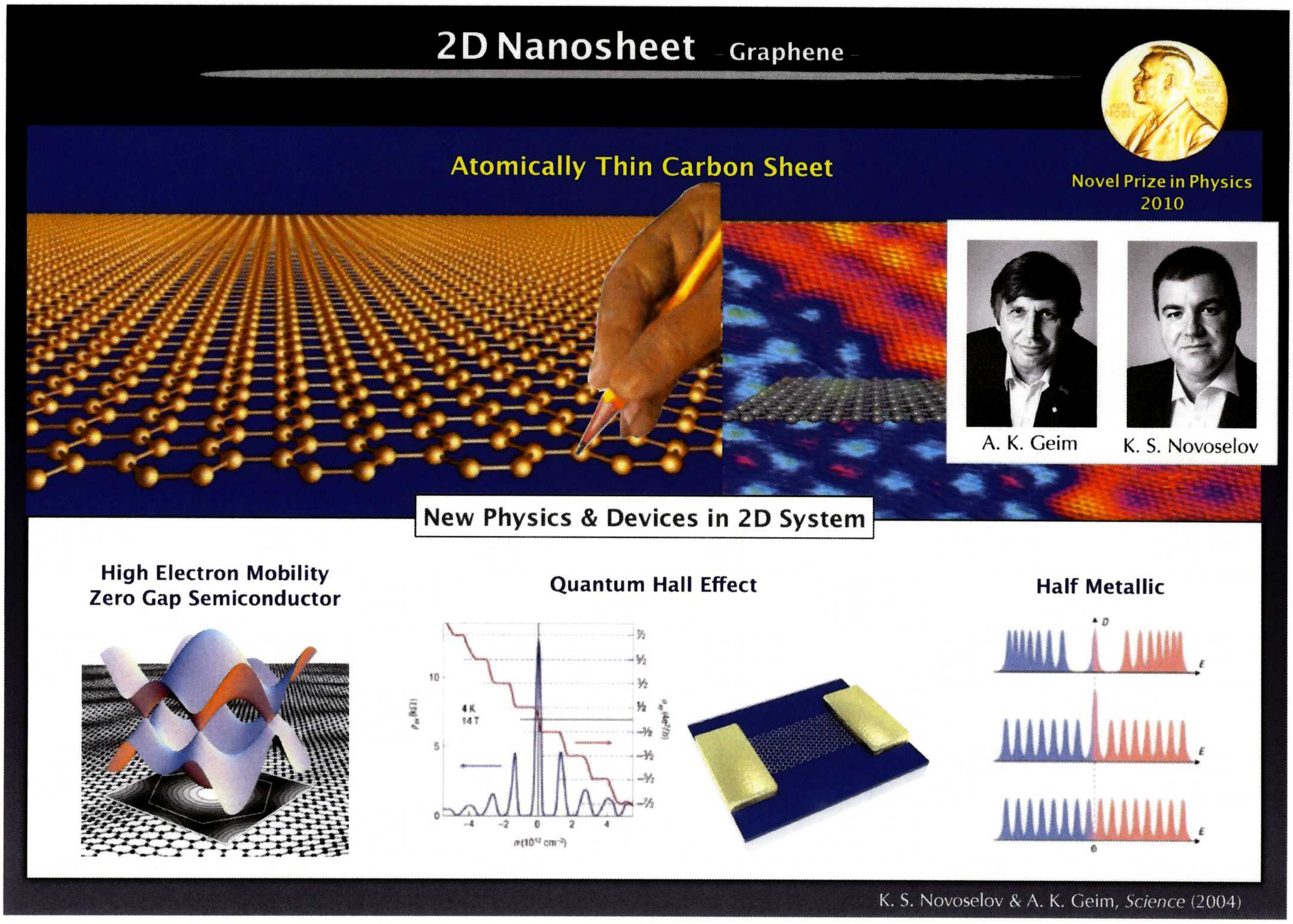
1. What is Oxide Nanosheet?

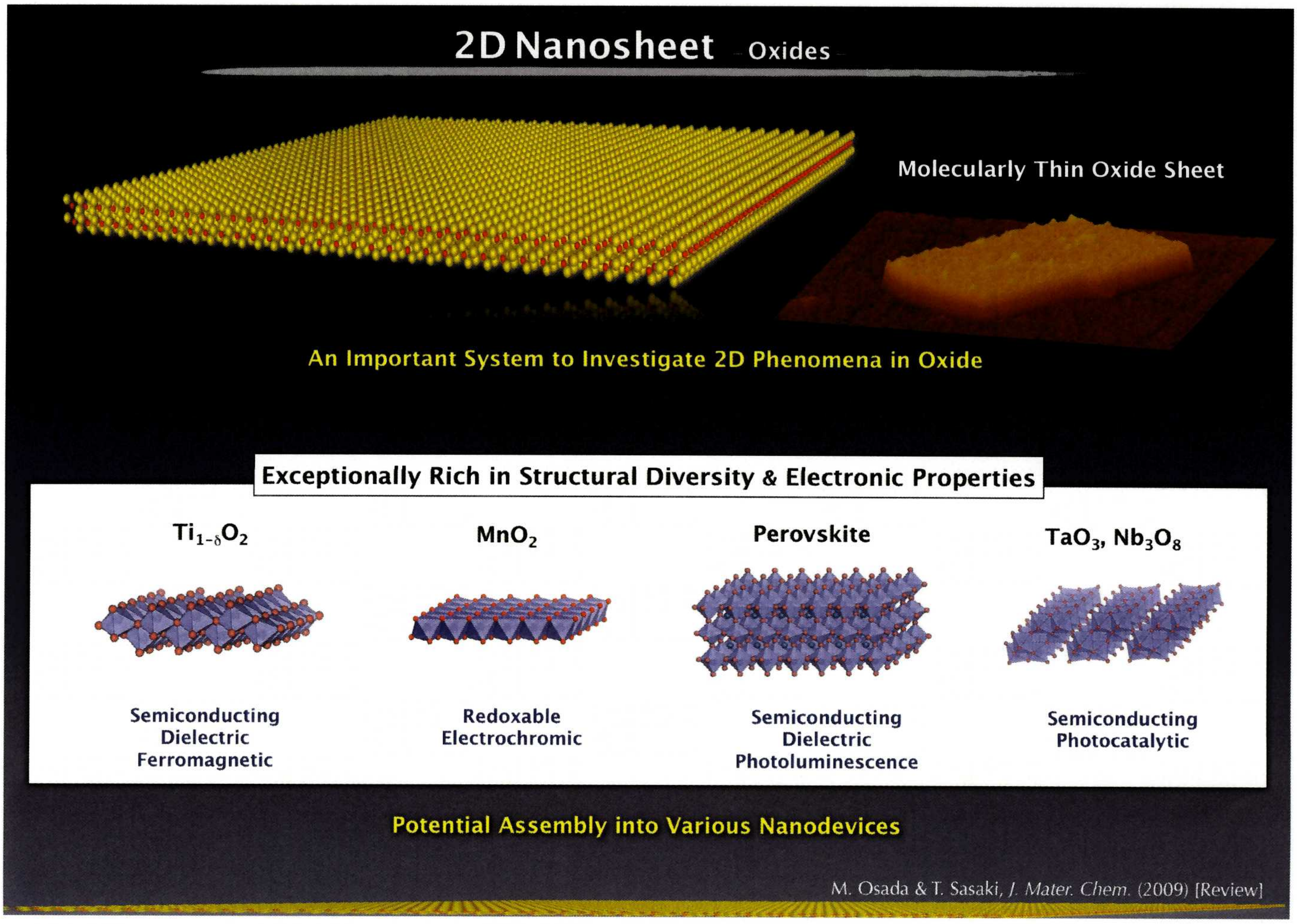
2. Materials Synthesis Using Oxide Nanosheets

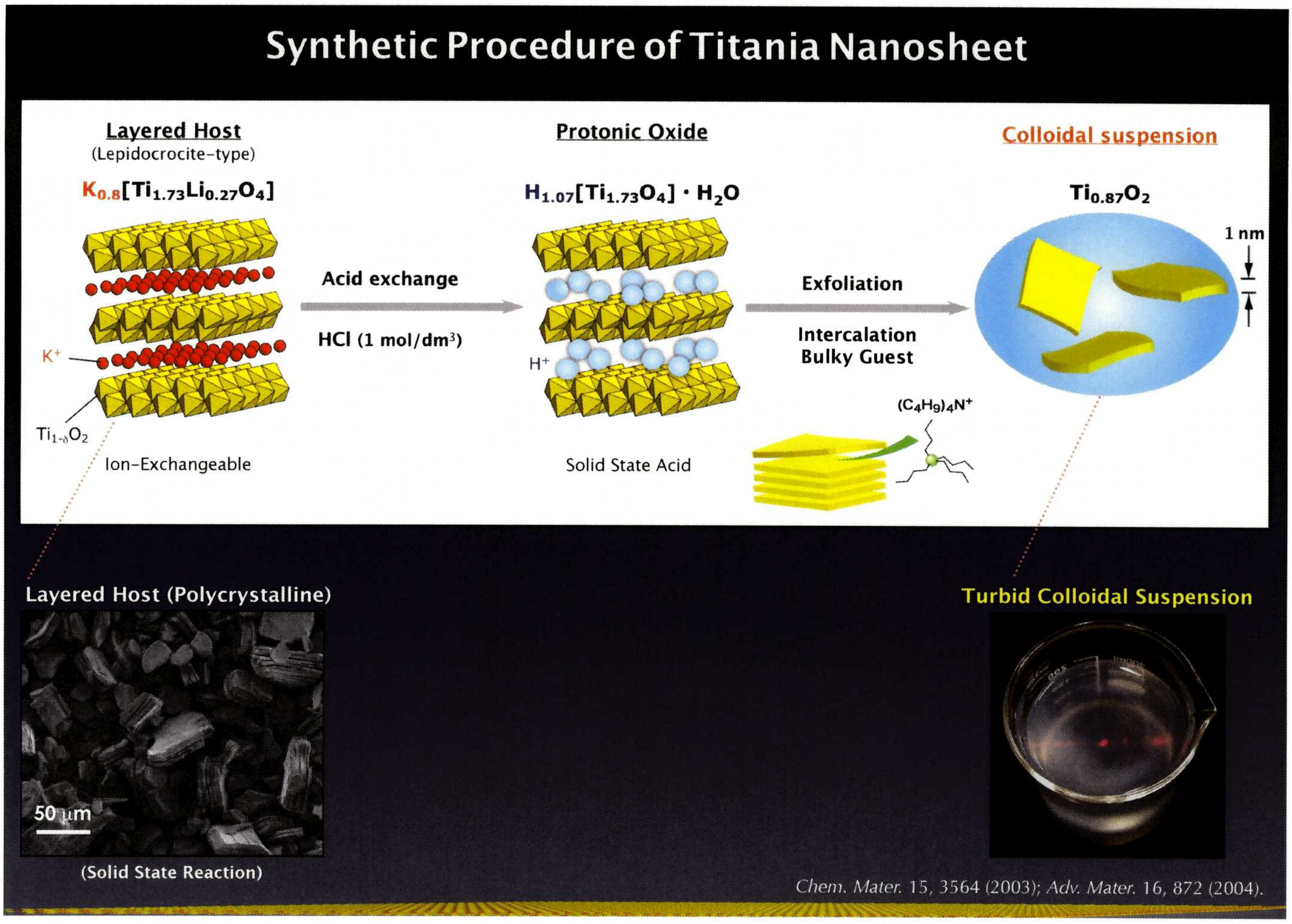
3. Application to Nanoelectronics

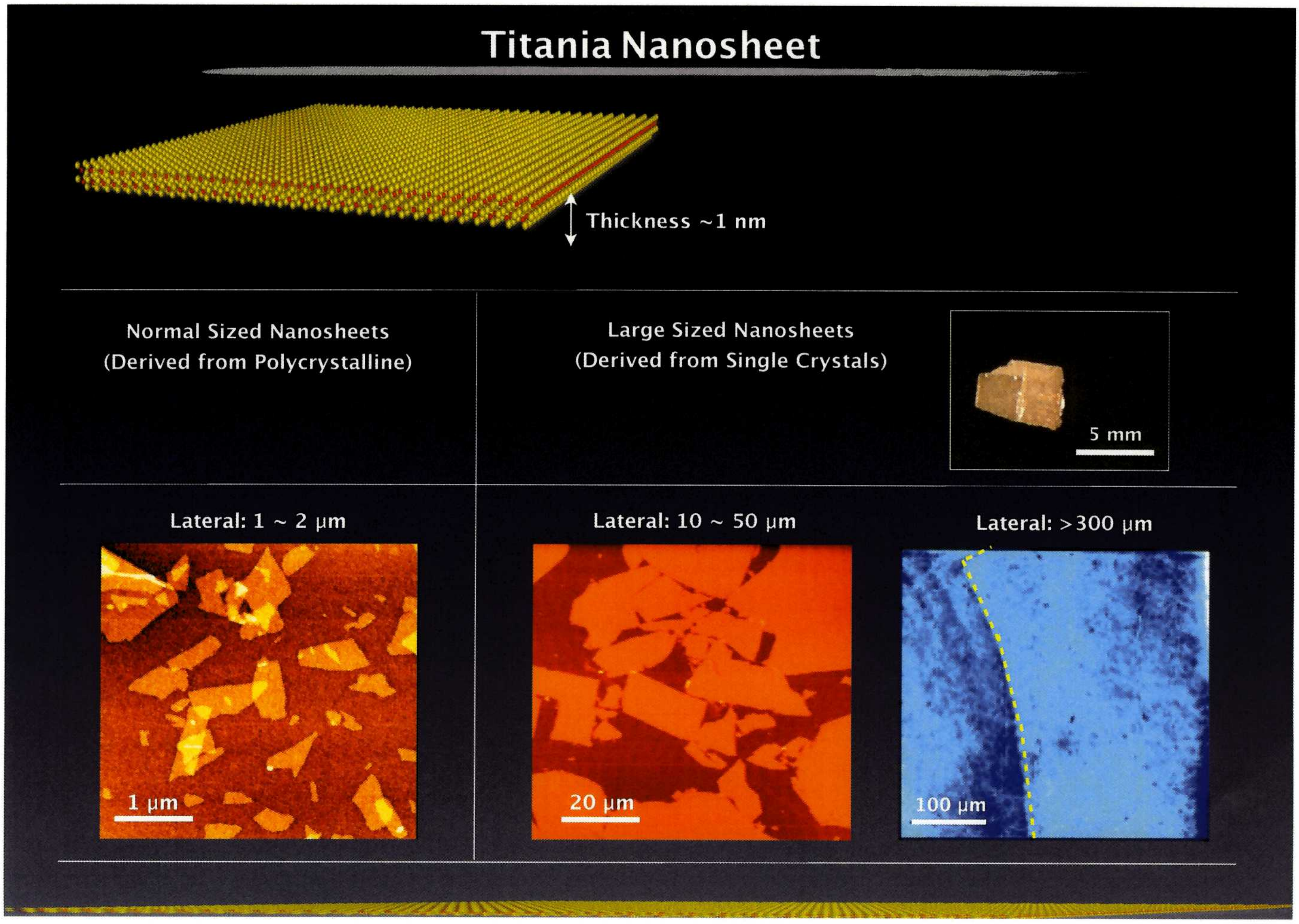

Oxide Nanosheet – A New Class of 2D Nanomaterials –
Layered Compound
Bulky Guest
~μm
~μm
Exfoliation
Colloidal Suspension
~1 nm
Nanosheet
Molecularly Thin Nanosheet
(Functional Nanoblock)
T. Sasaki et al., J. Am. Chem. Soc. 120, 4682 (1998)

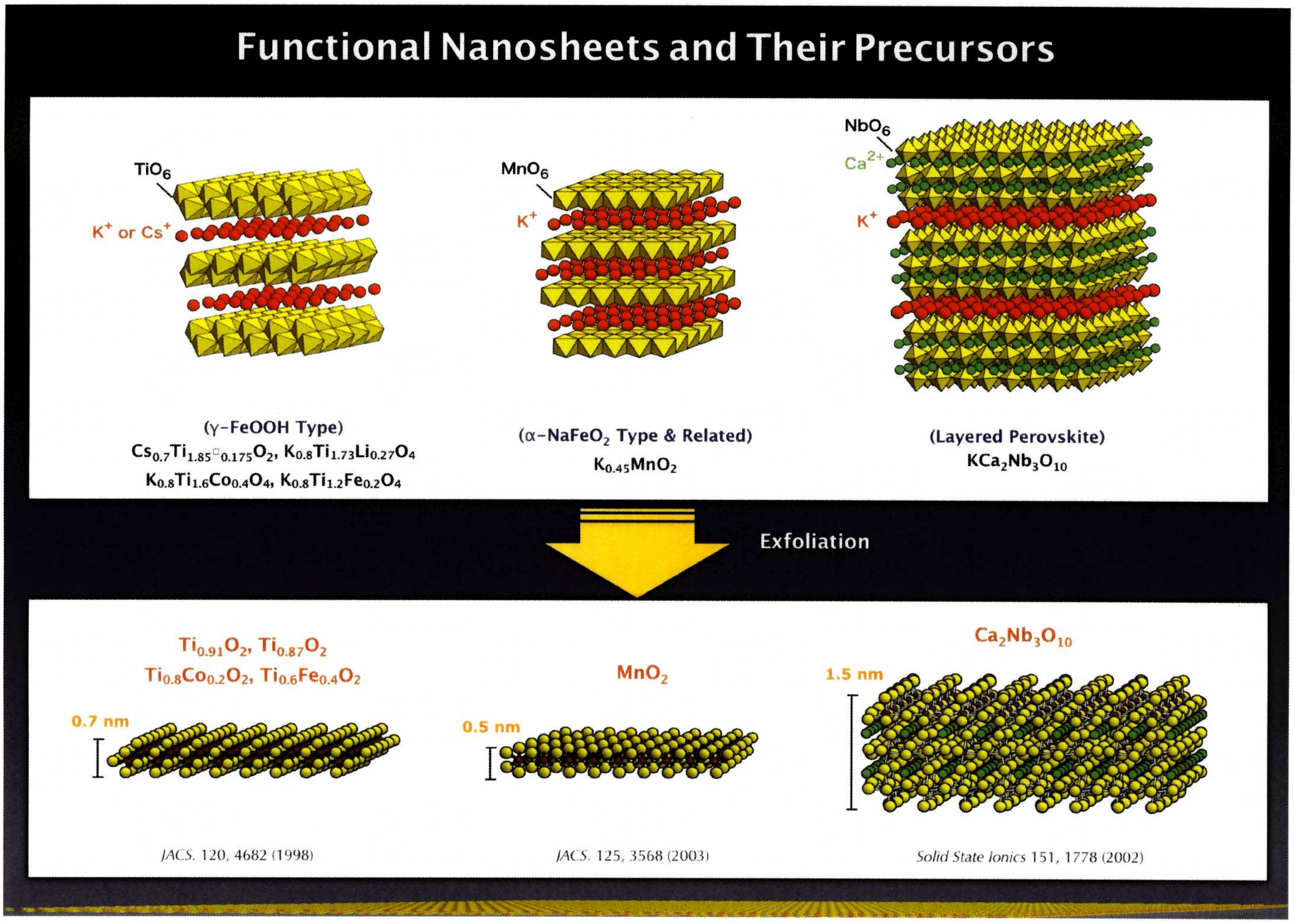

Oxide Nanosheets – New Functional Nanomaterials –
4 Atoms
O
Ti
Titania Nanosheet ($Ti_{1-\delta}O_2$)
Thickness ~1 nm
Lateral ~10 μm
Ultimate 2D Nature (Thickness ~1 nm, Lateral ~μm)
Thinnest Self-Standing Nanostructure in Oxide
2D Single Crystal (with Well-Defined Composition)
Keeping 2D Atomic Arrangement of Starting Compound
Novel Physical Properties in 2D System
Substantially Different from 3D Bulk System


2D Nanosheet - Graphene -
Atomically Thin Carbon Sheet
Novel Prize in Physics
2010
A. K. Geim
K. S. Novoselov
New Physics & Devices in 2D System
High Electron Mobility
Zero Gap Semiconductor
Quantum Hall Effect
Half Metallic
K. S. Novoselov & A. K. Geim, *Science* (2004)

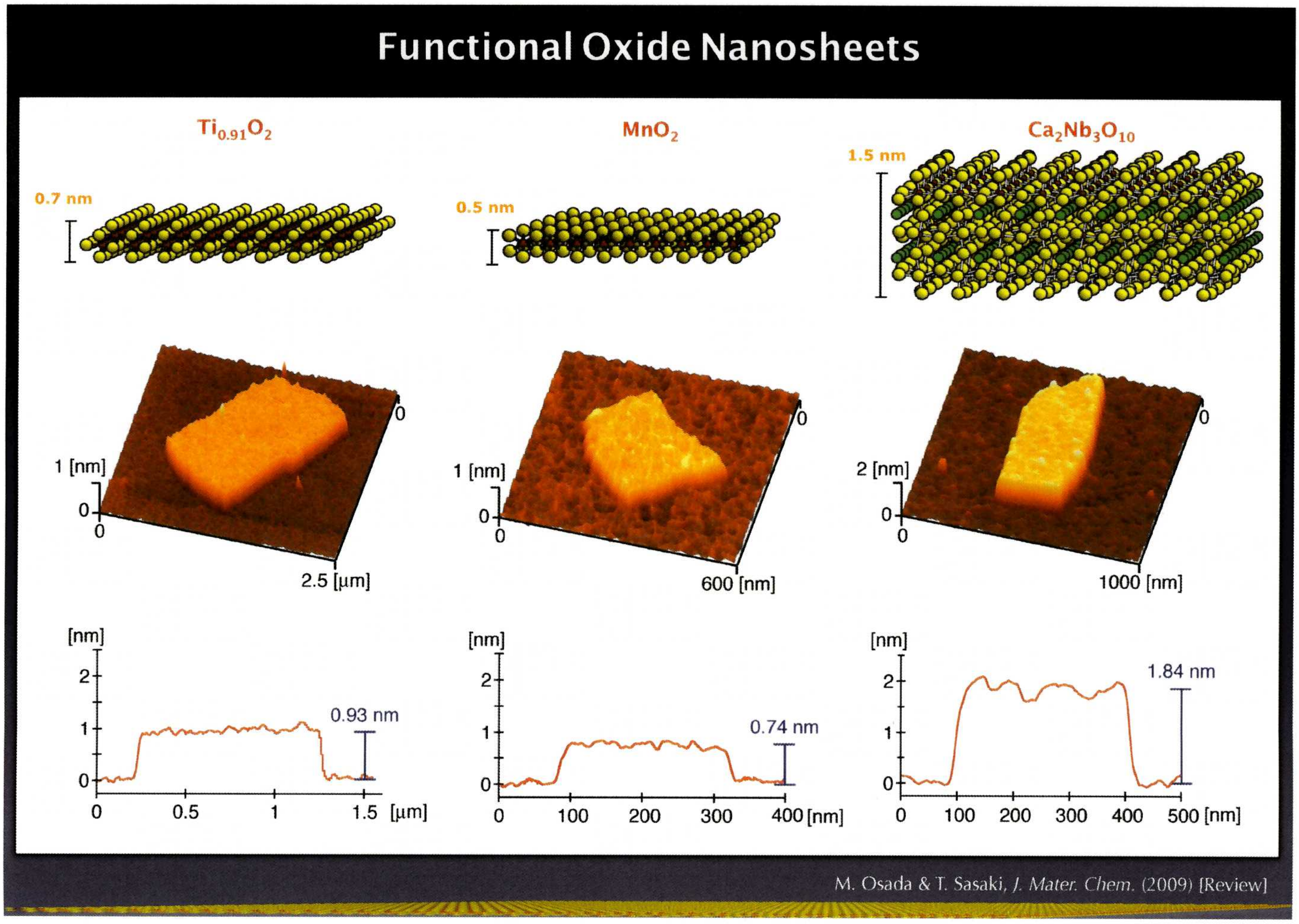

2D Nanosheet - Oxides -
Molecularly Thin Oxide Sheet
An Important System to Investigate 2D Phenomena in Oxide
Exceptionally Rich in Structural Diversity & Electronic Properties
$Ti_{1-\delta}O_2$
MnO_2
Perovskite
TaO_3, Nb_3O_8
Semiconducting
Dielectric
Ferromagnetic
Redoxable
Electrochromic
Semiconducting
Dielectric
Photoluminescence
Semiconducting
Photocatalytic
Potential Assembly into Various Nanodevices
M. Osada & T. Sasaki, *J. Mater. Chem.* (2009) [Review]


Synthetic Procedure of Titania Nanosheet
Layered Host
(Lepidocrocite-type)
$K_{0.8}[Ti_{1.73}Li_{0.27}O_4]$
K+
$Ti_{1-\delta}O_2$
Ion-Exchangeable
Acid exchange
HCl (1 mol/dm³)
Protonic Oxide
$H_{1.07}[Ti_{1.73}O_4] \cdot H_2O$
H+
Solid State Acid
Exfoliation
Intercalation
Bulky Guest
$(C_4H_9)_4N^+$
Colloidal suspension
$Ti_{0.87}O_2$
1 nm
Layered Host (Polycrystalline)
50 μm
(Solid State Reaction)
Turbid Colloidal Suspension
Chem. Mater. 15, 3564 (2003); Adv. Mater. 16, 872 (2004).

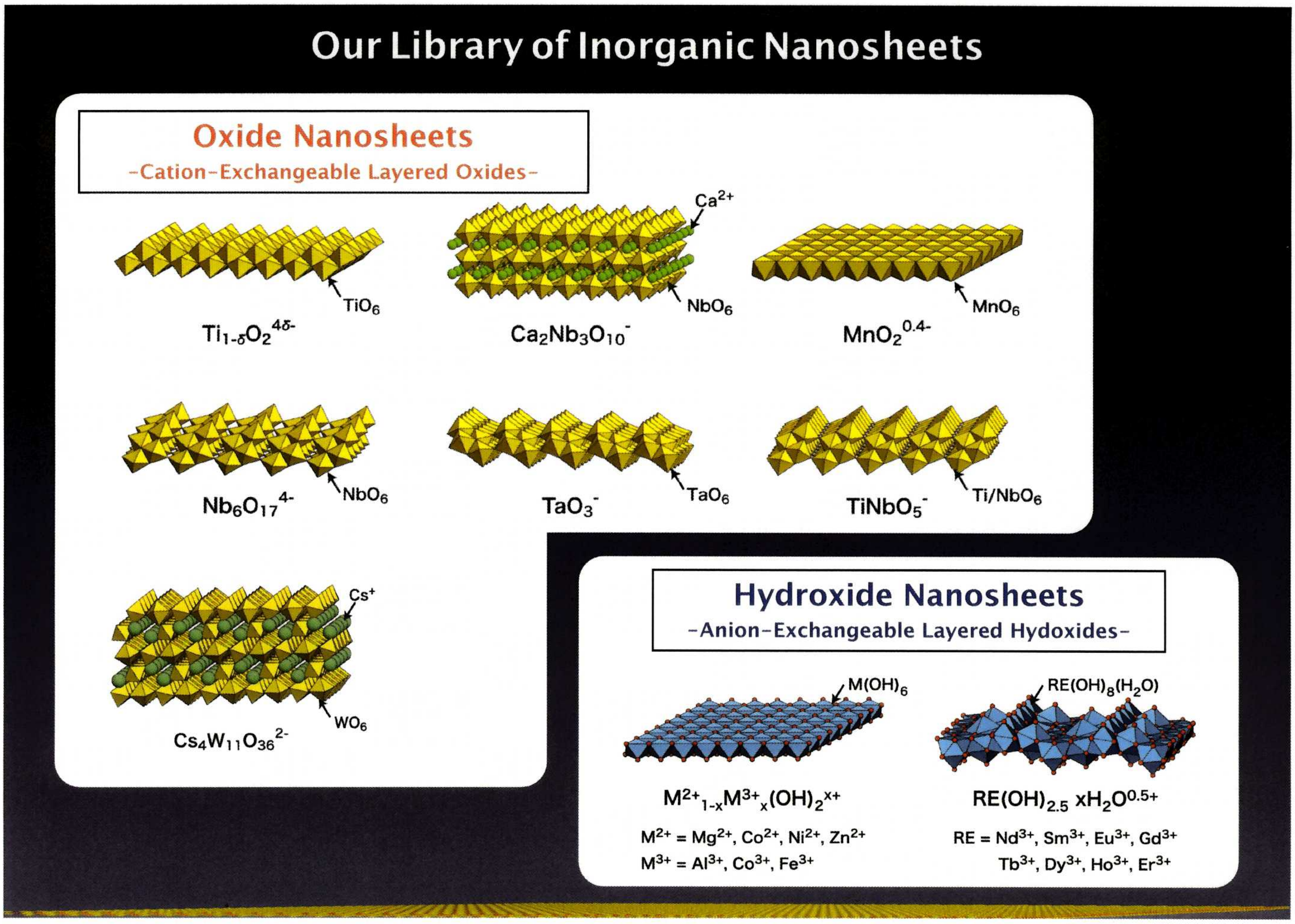

Titania Nanosheet
Thickness ~1 nm
Normal Sized Nanosheets
(Derived from Polycrystalline)
Large Sized Nanosheets
(Derived from Single Crystals)
5 mm
Lateral: 1 ~ 2 μm
1 μm
Lateral: 10 ~ 50 μm
20 μm
Lateral: >300 μm
100 μm

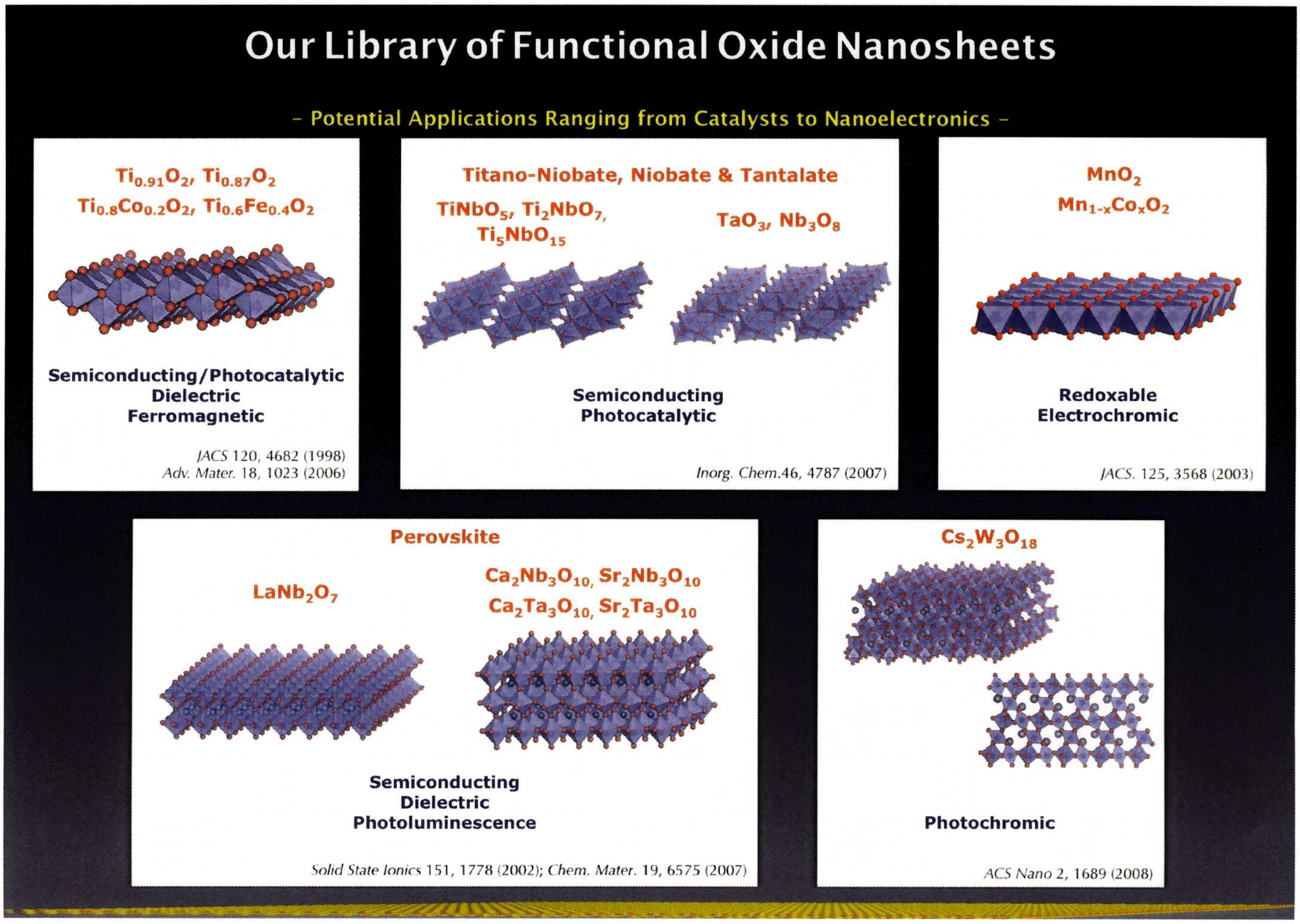


Functional Nanosheets and Their Precursors
TiO_6
K^+ or Cs^+
MnO_6
K^+
NbO_6
Ca^{2+}
K^+
(γ-FeOOH Type)
$Cs_{0.7}Ti_{1.85}\square_{0.175}O_2$, $K_{0.8}Ti_{1.73}Li_{0.27}O_4$
$K_{0.8}Ti_{1.6}Co_{0.4}O_4$, $K_{0.8}Ti_{1.2}Fe_{0.2}O_4$
(α-$NaFeO_2$ Type & Related)
$K_{0.45}MnO_2$
(Layered Perovskite)
$KCa_2Nb_3O_{10}$
Exfoliation
$Ti_{0.91}O_2$, $Ti_{0.87}O_2$
$Ti_{0.8}Co_{0.2}O_2$, $Ti_{0.6}Fe_{0.4}O_2$
0.7 nm
MnO_2
0.5 nm
$Ca_2Nb_3O_{10}$
1.5 nm
JACS. 120, 4682 (1998)
JACS. 125, 3568 (2003)
Solid State Ionics 151, 1778 (2002)



Functional Oxide Nanosheets
$Ti_{0.91}O_2$
0.7 nm
MnO_2
0.5 nm
$Ca_2Nb_3O_{10}$
1.5 nm
1 [nm]
0
0
2.5 [μm]
1 [nm]
0
0
600 [nm]
2 [nm]
0
0
1000 [nm]
[nm]
2
1
0
0 0.5 1 1.5 [μm]
0.93 nm
[nm]
2
1
0
0 100 200 300 400 [nm]
0.74 nm
[nm]
2
1
0
0 100 200 300 400 500 [nm]
1.84 nm
M. Osada & T. Sasaki, J. Mater. Chem. (2009) [Review]


Our Library of Inorganic Nanosheets
Oxide Nanosheets
-Cation-Exchangeable Layered Oxides-
TiO_6
$Ti_{1-\delta}O_2^{4\delta-}$
Ca^{2+}
NbO_6
$Ca_2Nb_3O_{10}^-$
MnO_6
$MnO_2^{0.4-}$
NbO_6
$Nb_6O_{17}^{4-}$
TaO_6
TaO_3^-
Ti/NbO_6
$TiNbO_5^-$
Cs^+
WO_6
$Cs_4W_{11}O_{36}^{2-}$
Hydroxide Nanosheets
-Anion-Exchangeable Layered Hydoxides-
$M(OH)_6$
$RE(OH)_8(H_2O)$
$M^{2+}_{1-x}M^{3+}_x(OH)_2^{x+}$
$M^{2+} = Mg^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}$
$M^{3+} = Al^{3+}, Co^{3+}, Fe^{3+}$
$RE(OH)_{2.5}\ xH_2O^{0.5+}$
$RE = Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}$
$Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}$


Our Library of Functional Oxide Nanosheets
- Potential Applications Ranging from Catalysts to Nanoelectronics -
$Ti_{0.91}O_2$, $Ti_{0.87}O_2$
$Ti_{0.8}Co_{0.2}O_2$, $Ti_{0.6}Fe_{0.4}O_2$
Semiconducting/Photocatalytic
Dielectric
Ferromagnetic
JACS 120, 4682 (1998)
Adv. Mater. 18, 1023 (2006)
Titano-Niobate, Niobate & Tantalate
$TiNbO_5$, Ti_2NbO_7,
Ti_5NbO_{15}
TaO_3, Nb_3O_8
Semiconducting
Photocatalytic
Inorg. Chem.46, 4787 (2007)
MnO_2
$Mn_{1-x}Co_xO_2$
Redoxable
Electrochromic
JACS. 125, 3568 (2003)
Perovskite
$LaNb_2O_7$
$Ca_2Nb_3O_{10}$, $Sr_2Nb_3O_{10}$
$Ca_2Ta_3O_{10}$, $Sr_2Ta_3O_{10}$
Semiconducting
Dielectric
Photoluminescence
Solid State Ionics 151, 1778 (2002); Chem. Mater. 19, 6575 (2007)
$Cs_2W_3O_{18}$
Photochromic
ACS Nano 2, 1689 (2008)

Outline

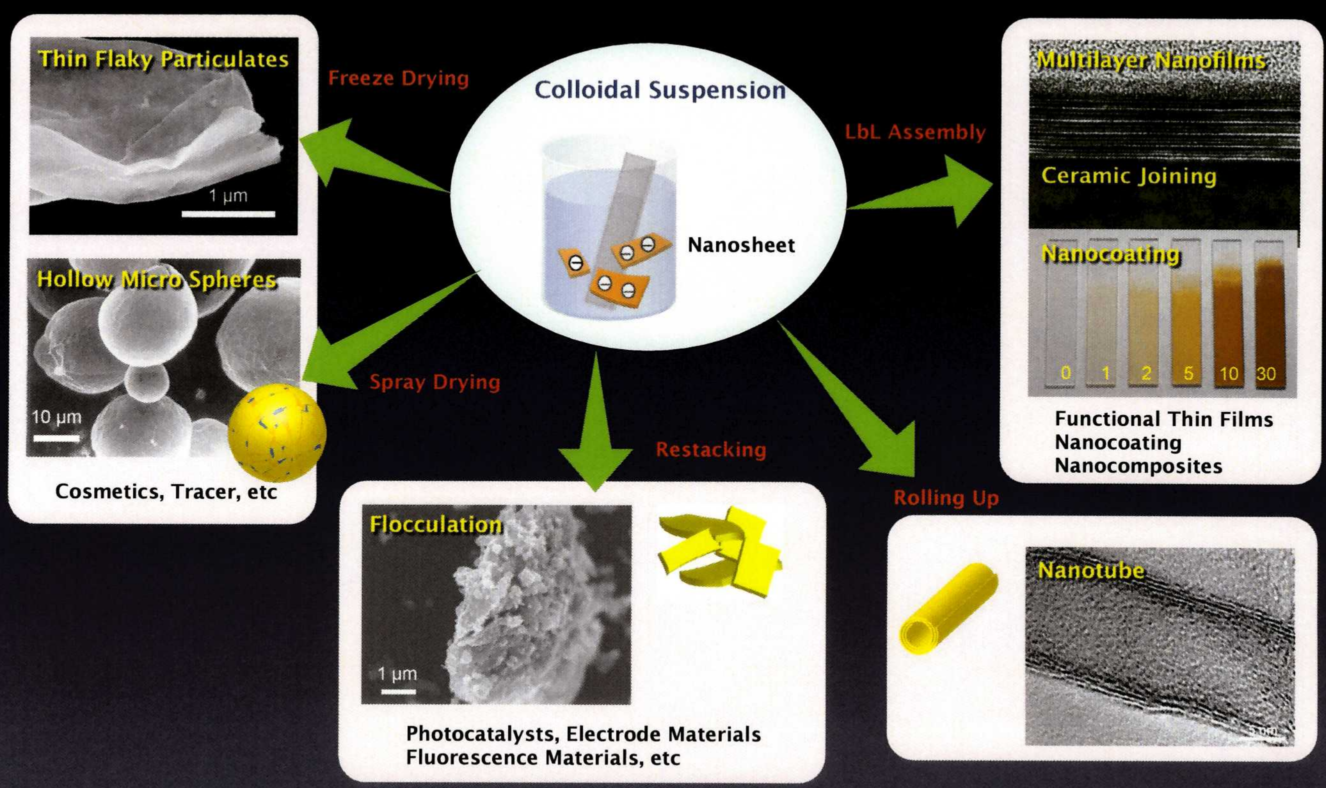
1. What is Oxide Nanosheet?

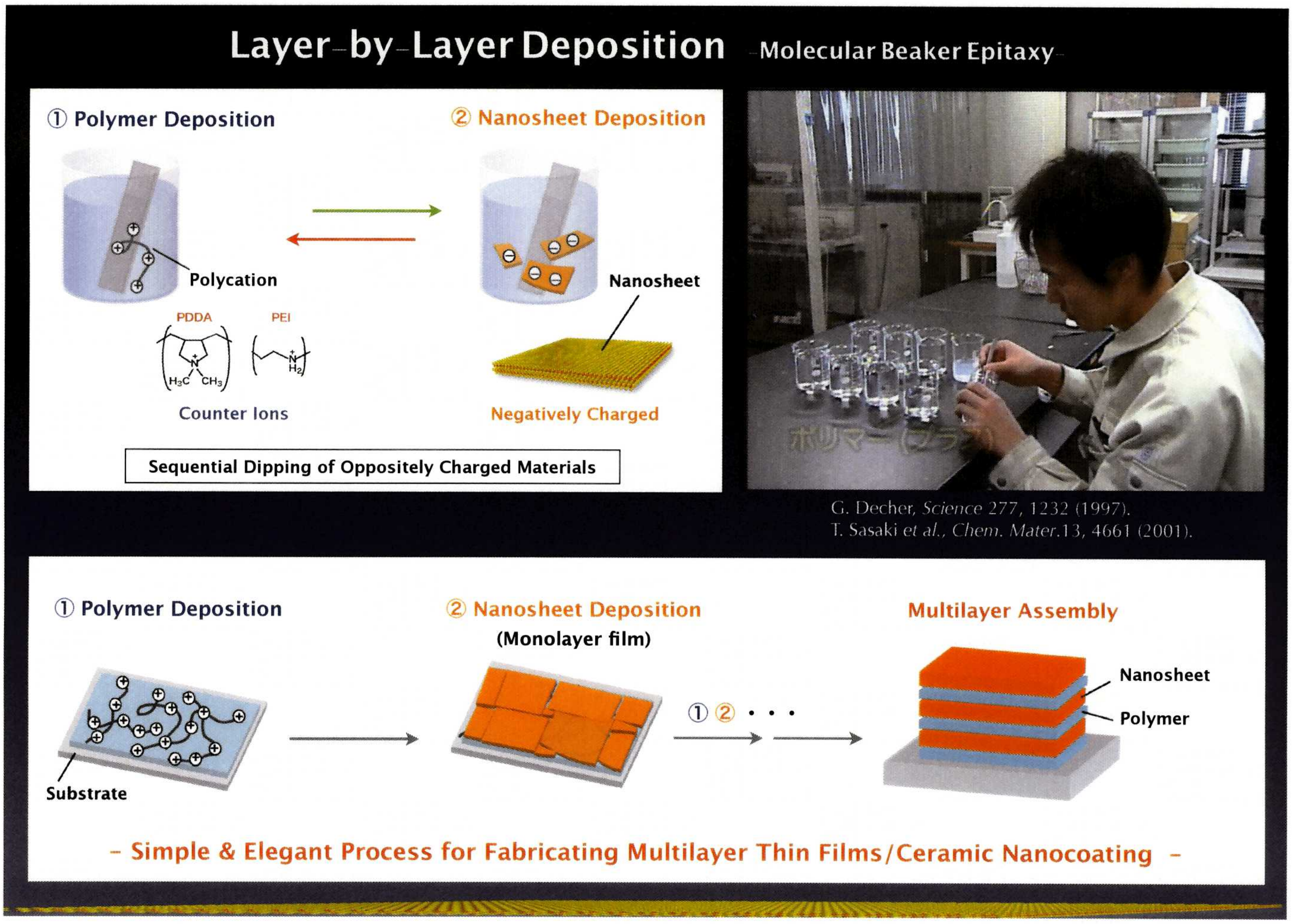
2. Materials Synthesis Using Oxide Nanosheets

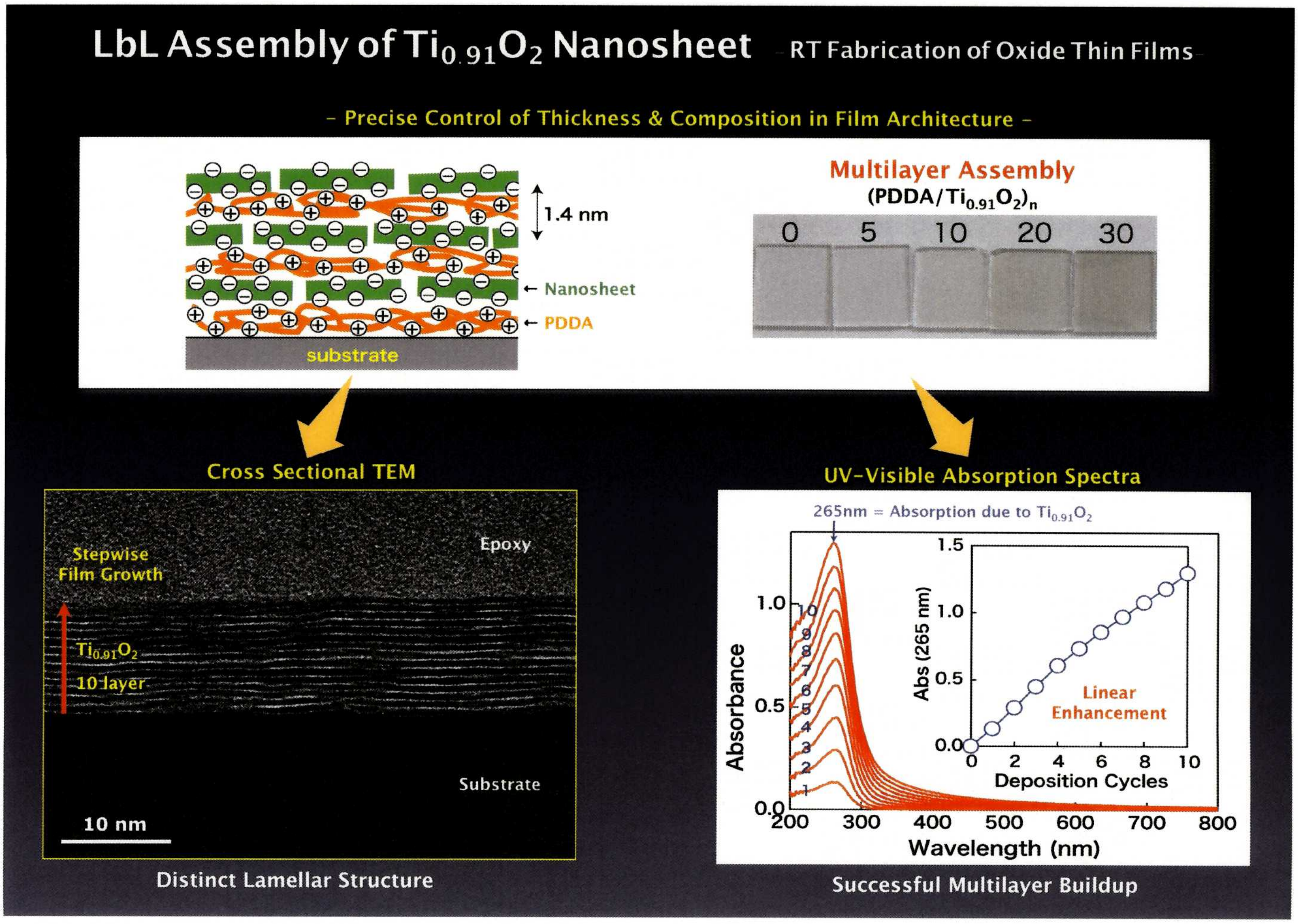
3. Application to Nanoelectronics

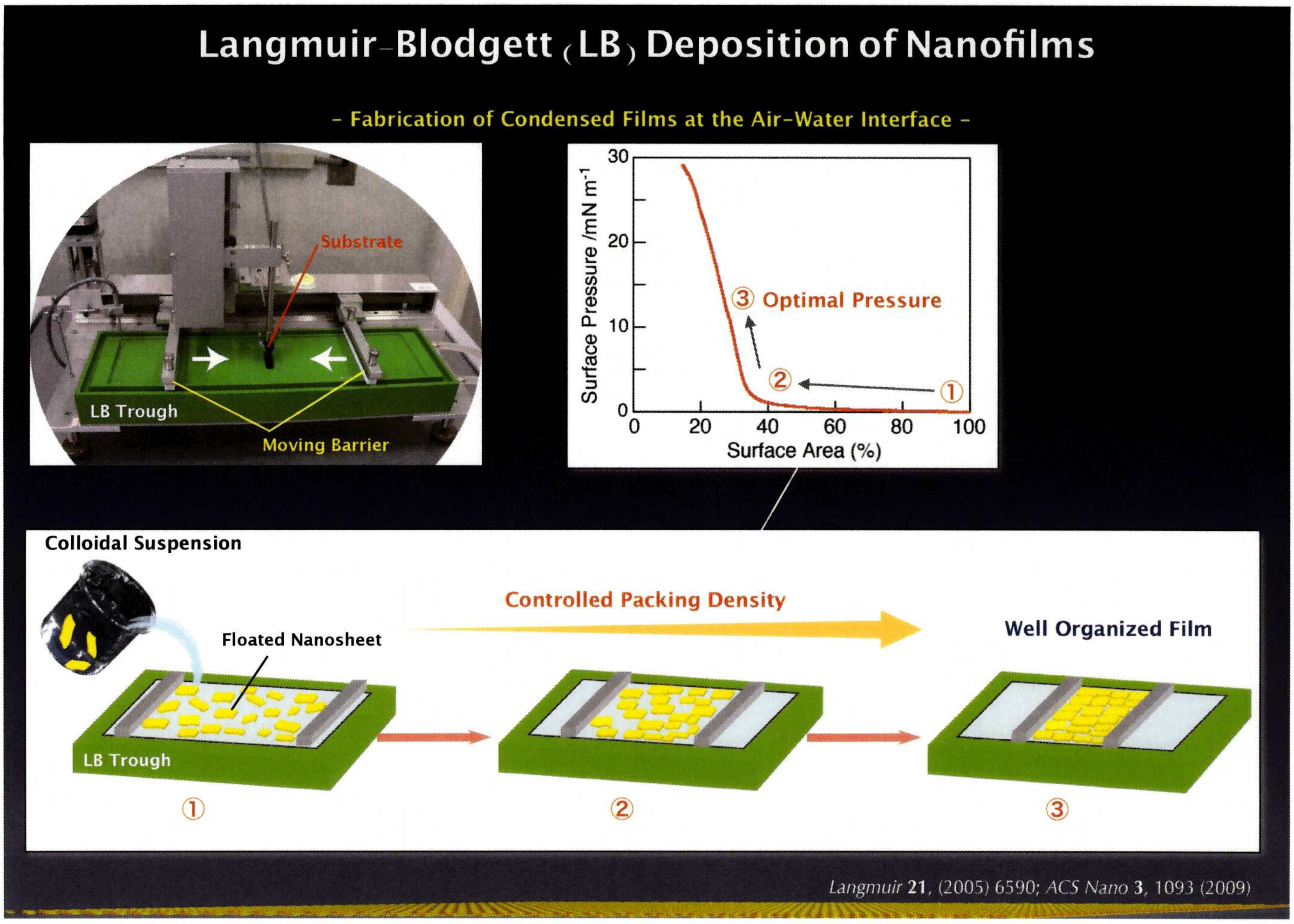
Smart Materials Synthesis Using Oxide Nanosheets

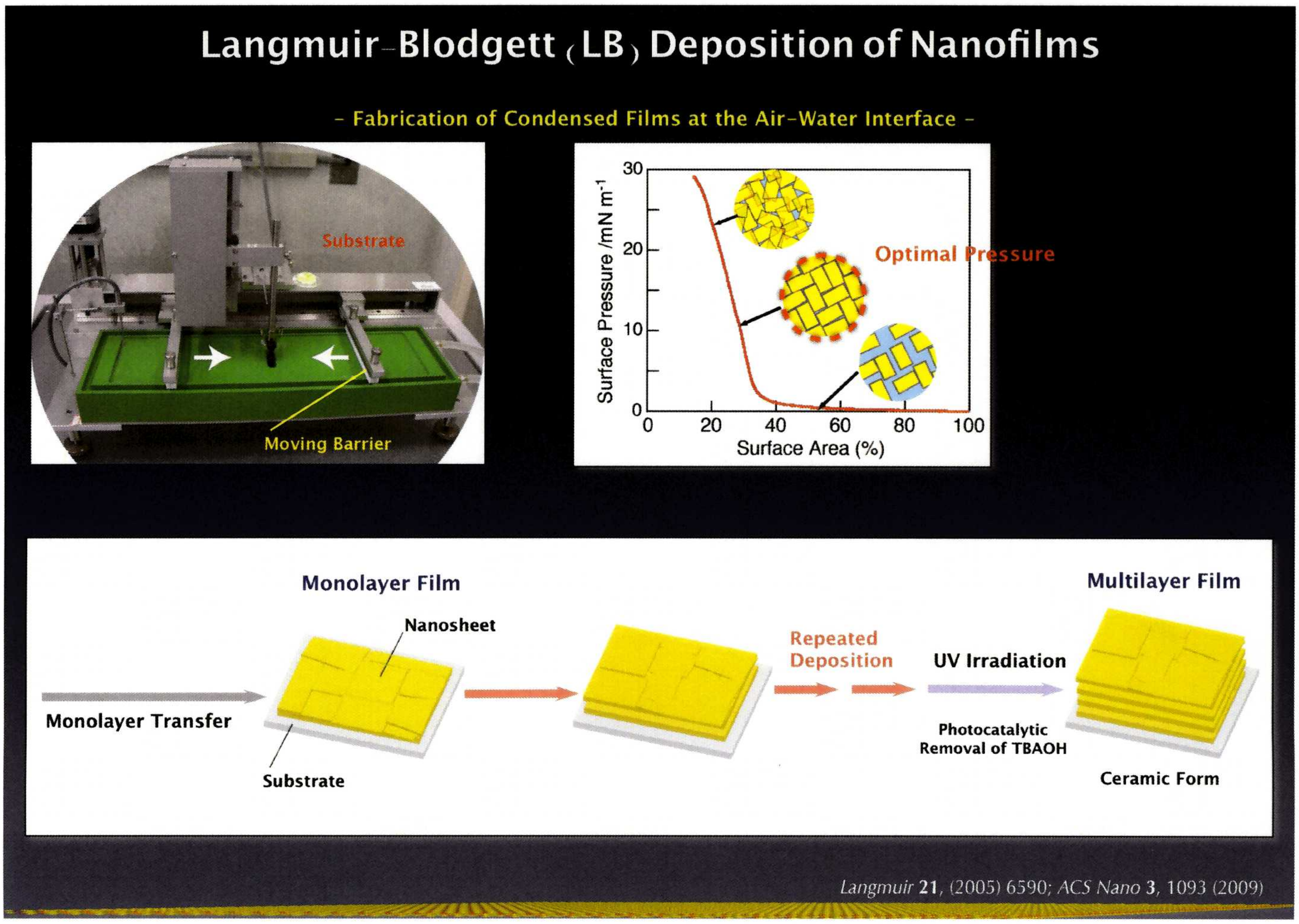
Organization, Assembly & Shape-Control in Nano to Micrometer Range

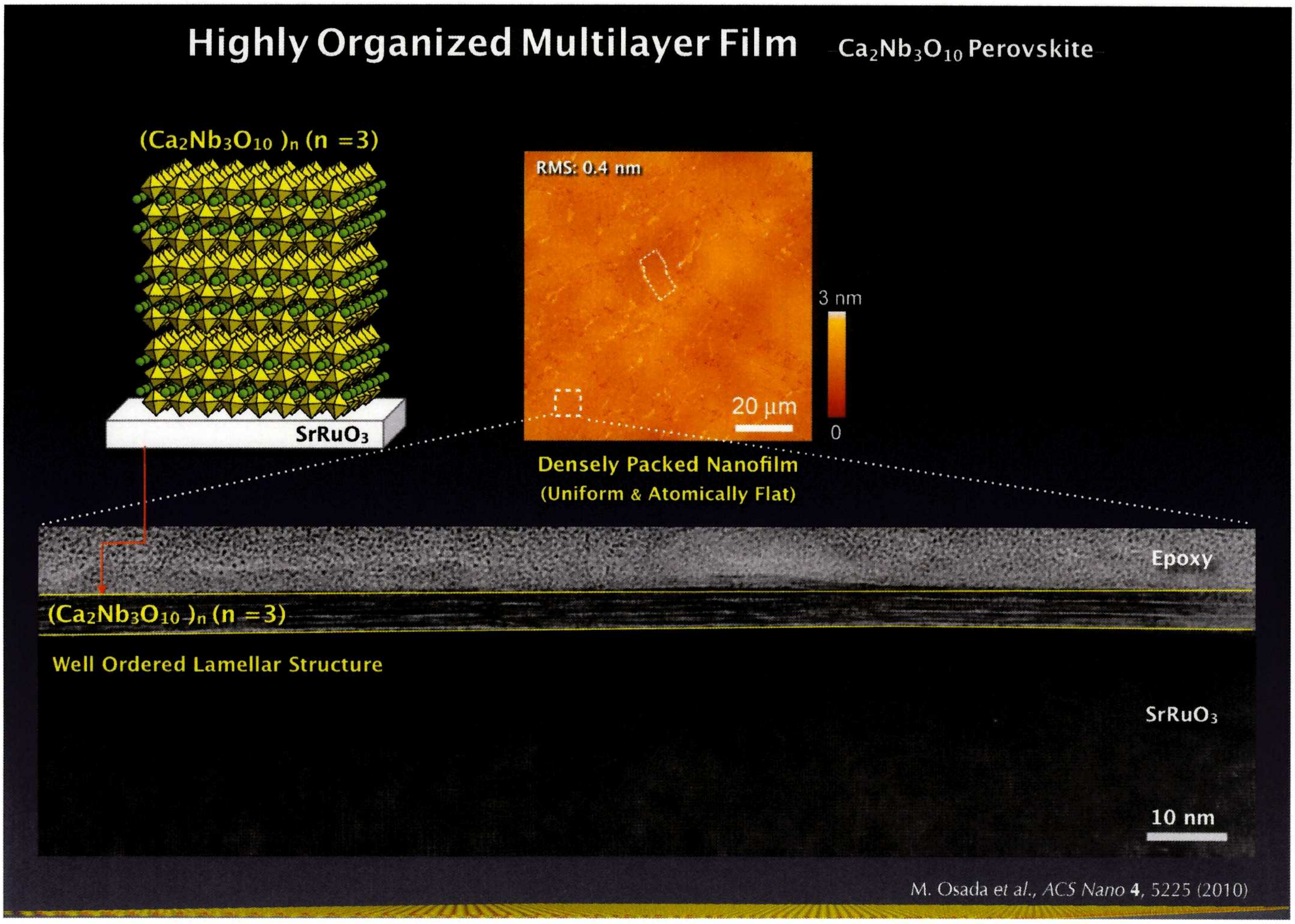


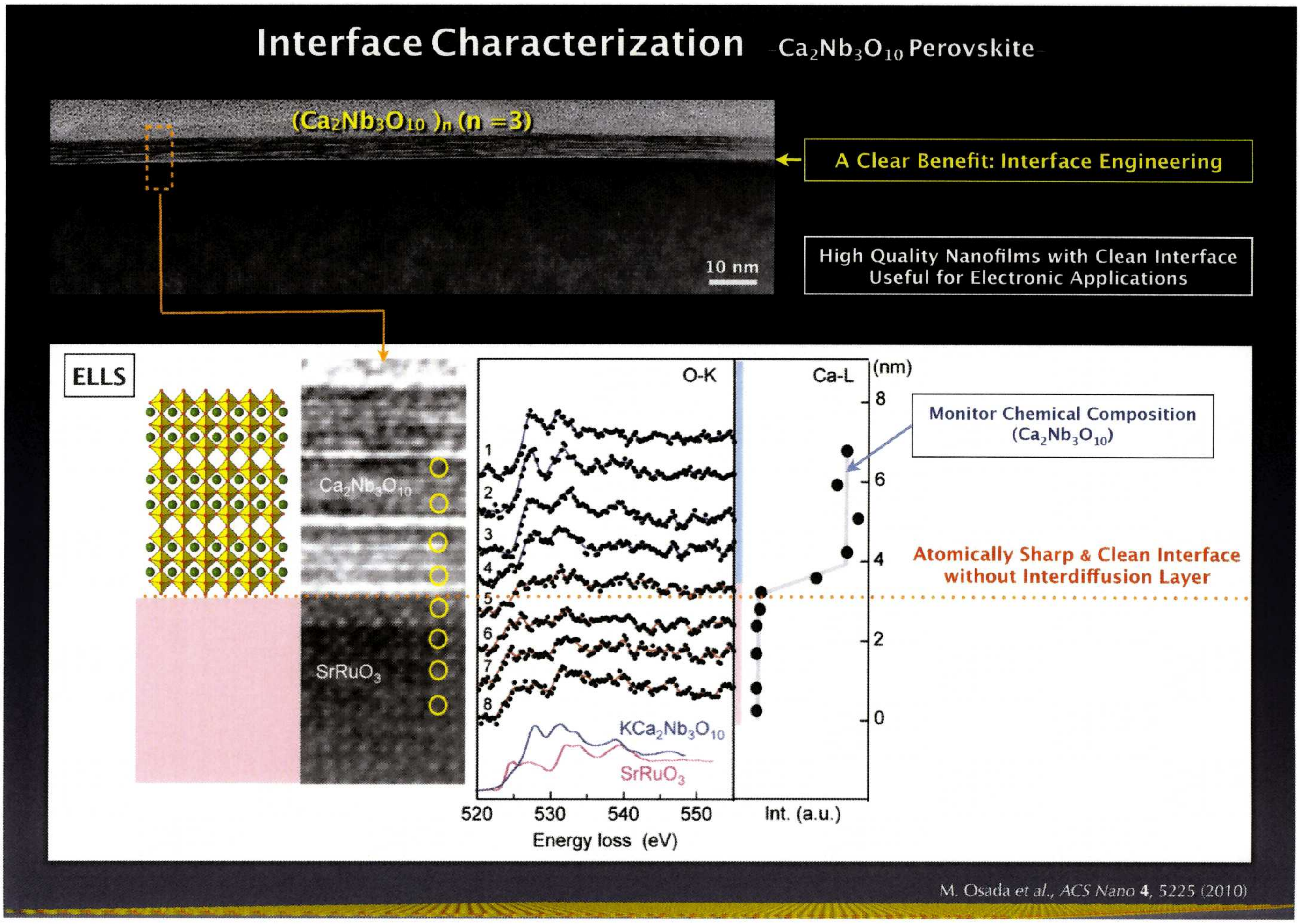

Layer-by-Layer Deposition
Molecular Beaker Epitaxy
① Polymer Deposition
② Nanosheet Deposition
Polycation
Nanosheet
PDDA
PEI
Counter Ions
Negatively Charged
Sequential Dipping of Oppositely Charged Materials
G. Decher, Science 277, 1232 (1997).
T. Sasaki et al., Chem. Mater.13, 4661 (2001).
① Polymer Deposition
② Nanosheet Deposition
(Monolayer film)
Multilayer Assembly
Substrate
① ② · · ·
Nanosheet
Polymer
– Simple & Elegant Process for Fabricating Multilayer Thin Films/Ceramic Nanocoating –

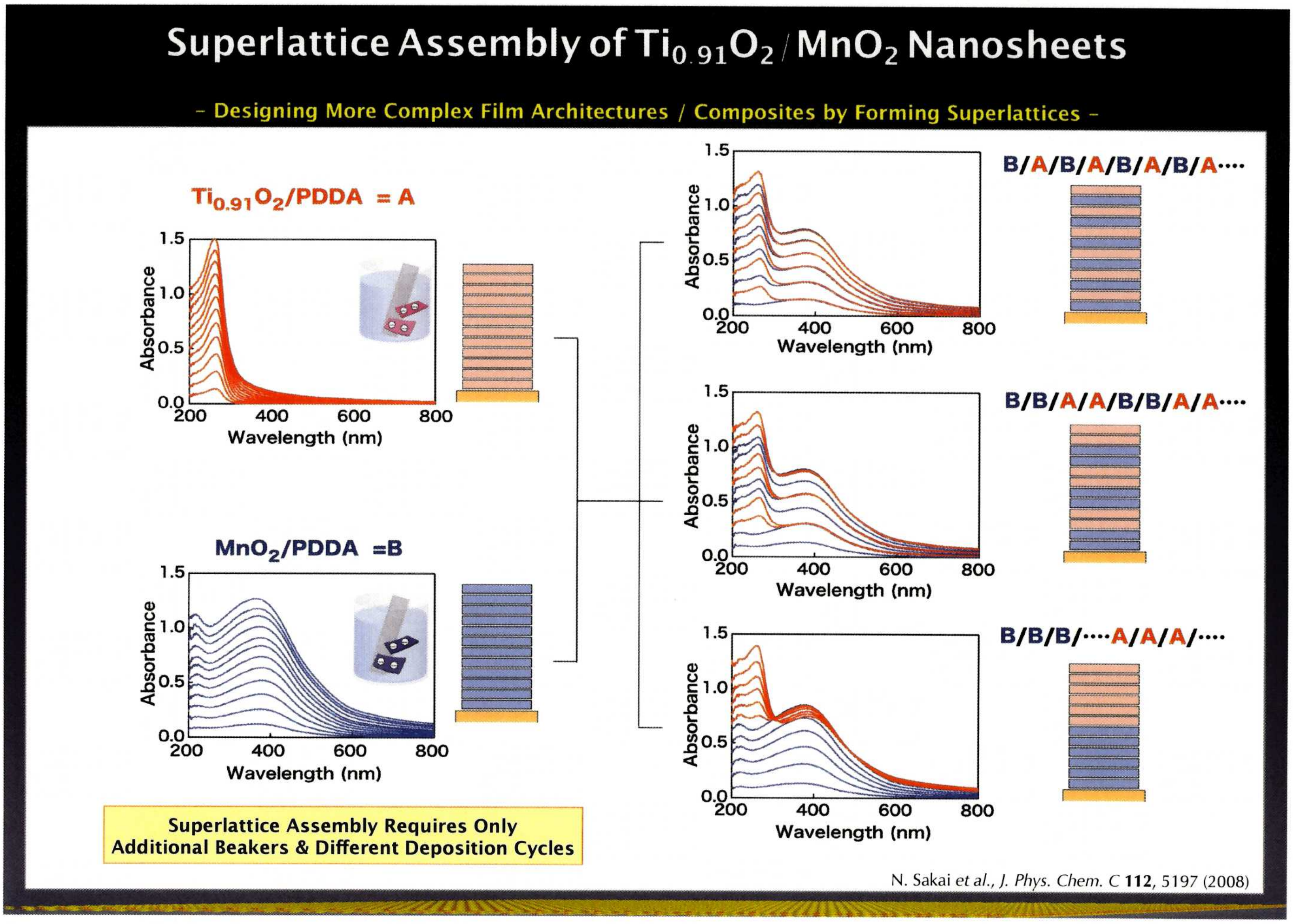

LbL Assembly of $Ti_{0.91}O_2$ Nanosheet
RT Fabrication of Oxide Thin Films
– Precise Control of Thickness & Composition in Film Architecture –
1.4 nm
Nanosheet
PDDA
substrate
Multilayer Assembly
$(PDDA/Ti_{0.91}O_2)_n$
0 5 10 20 30
Cross Sectional TEM
Epoxy
Stepwise Film Growth
$Ti_{0.91}O_2$
10 layer
Substrate
10 nm
Distinct Lamellar Structure
UV-Visible Absorption Spectra
265nm = Absorption due to $Ti_{0.91}O_2$
Absorbance
Wavelength (nm)
Abs (265 nm)
Deposition Cycles
Linear Enhancement
Successful Multilayer Buildup

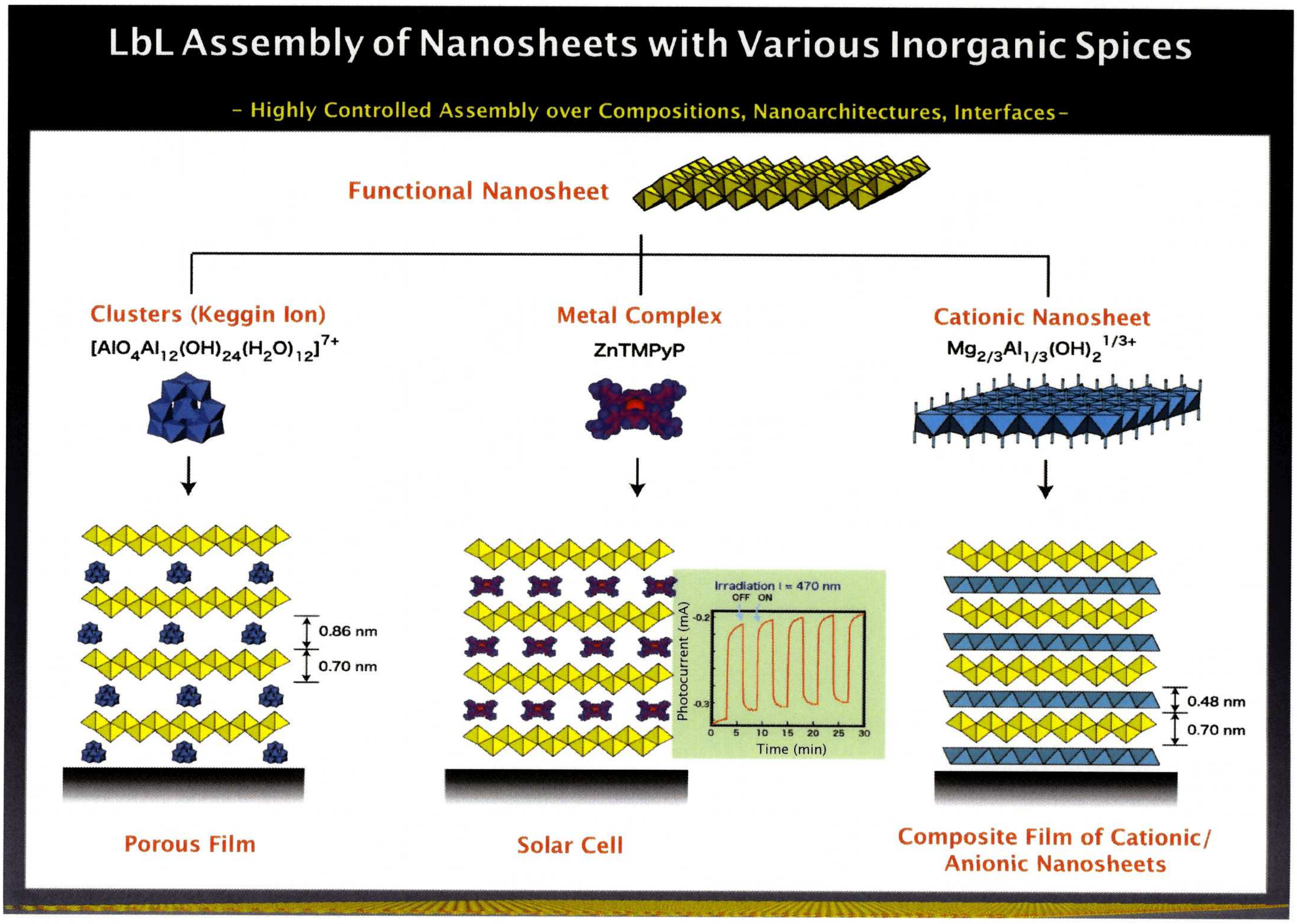

Langmuir–Blodgett (LB) Deposition of Nanofilms
– Fabrication of Condensed Films at the Air-Water Interface –
Substrate
LB Trough
Moving Barrier
Surface Pressure /mN m⁻¹
Surface Area (%)
0
20
40
60
80
100
10
30
③ Optimal Pressure
②
①
Colloidal Suspension
Floated Nanosheet
Controlled Packing Density
Well Organized Film
LB Trough
①
②
③
Langmuir 21, (2005) 6590; ACS Nano 3, 1093 (2009)


Langmuir–Blodgett (LB) Deposition of Nanofilms
– Fabrication of Condensed Films at the Air-Water Interface –
Substrate
Moving Barrier
Surface Pressure /mN m⁻¹
Surface Area (%)
0
20
40
60
80
100
10
30
Optimal Pressure
Monolayer Film
Nanosheet
Monolayer Transfer
Substrate
Repeated Deposition
UV Irradiation
Photocatalytic Removal of TBAOH
Multilayer Film
Ceramic Form
Langmuir 21, (2005) 6590; ACS Nano 3, 1093 (2009)

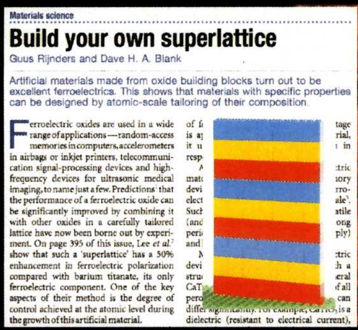

Highly Organized Multilayer Film
$Ca_2Nb_3O_{10}$ Perovskite
$(Ca_2Nb_3O_{10})_n$ (n =3)
SrRuO3
RMS: 0.4 nm
3 nm
0
20 µm
Densely Packed Nanofilm
(Uniform & Atomically Flat)
Epoxy
$(Ca_2Nb_3O_{10})_n$ (n =3)
Well Ordered Lamellar Structure
$SrRuO_3$
10 nm
M. Osada et al., ACS Nano 4, 5225 (2010)


Interface Characterization
$Ca_2Nb_3O_{10}$ Perovskite
$(Ca_2Nb_3O_{10})_n$ (n =3)
A Clear Benefit: Interface Engineering
10 nm
High Quality Nanofilms with Clean Interface
Useful for Electronic Applications
ELLS
$Ca_2Nb_3O_{10}$
$SrRuO_3$
O-K
Ca-L
(nm)
$KCa_2Nb_3O_{10}$
$SrRuO_3$
Energy loss (eV)
Int. (a.u.)
Monitor Chemical Composition
$(Ca_2Nb_3O_{10})$
Atomically Sharp & Clean Interface
without Interdiffusion Layer
M. Osada et al., ACS Nano 4, 5225 (2010)


Superlattice Assembly of $Ti_{0.91}O_2$ / MnO_2 Nanosheets
- Designing More Complex Film Architectures / Composites by Forming Superlattices -
$Ti_{0.91}O_2$/PDDA = A
MnO_2/PDDA =B
Absorbance
Wavelength (nm)
B/A/B/A/B/A/B/A····
B/B/A/A/B/B/A/A····
B/B/B/····A/A/A/····
Superlattice Assembly Requires Only
Additional Beakers & Different Deposition Cycles
N. Sakai et al., J. Phys. Chem. C 112, 5197 (2008)


LbL Assembly of Nanosheets with Various Inorganic Spices
- Highly Controlled Assembly over Compositions, Nanoarchitectures, Interfaces-
Functional Nanosheet
Clusters (Keggin Ion)
$[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$
Metal Complex
ZnTMPyP
Cationic Nanosheet
$Mg_{2/3}Al_{1/3}(OH)_2^{1/3+}$
0.86 nm
0.70 nm
Irradiation λ = 470 nm
OFF ON
Photocurrent (mA)
Time (min)
0.48 nm
0.70 nm
Porous Film
Solar Cell
Composite Film of Cationic/
Anionic Nanosheets

Superlattice Approach in Oxide Thin Films



Materials science

Build your own superlattice

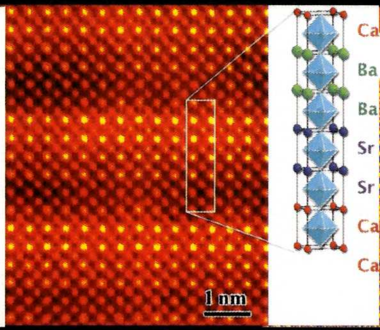
Guus Rijnders and Dave H. A. Blank

Artificial materials made from oxide building blocks turn out to be excellent ferroelectrics. This shows that materials with specific properties can be designed by atomic-scale tailoring of their composition.

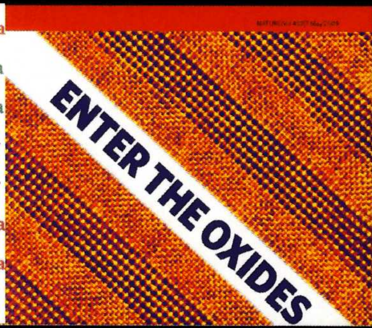
Ferroelectric oxides are used in a wide range of applications — random-access memories in computers, accelerometers in airbags or inkjet printers, telecommunication signal-processing devices and high-frequency devices for ultrasonic medical imaging, to name just a few. Predictions[1] that the performance of a ferroelectric oxide can be significantly improved by combining it with other oxides in a carefully tailored lattice have now been borne out by experiment. On page 395 of this issue, Lee *et al.*[2] show that such a 'superlattice' has a 50% enhancement in ferroelectric polarization compared with barium titanate, its only ferroelectric component. One of the key aspects of their method is the degree of control achieved at the atomic level during the growth of this artificial material.

dielectric (resistant to electrical current),

Nature **433**, 369 (2005)



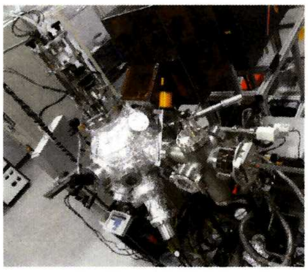
Nature **433**, 395 (2005)



Nature **459**, 28 (2009)

<Current Technique>

Atomic Layer Deposition / Molecular Beam Epitaxy



Fabrication of various complex oxide films

<New Thin-Film Technology>

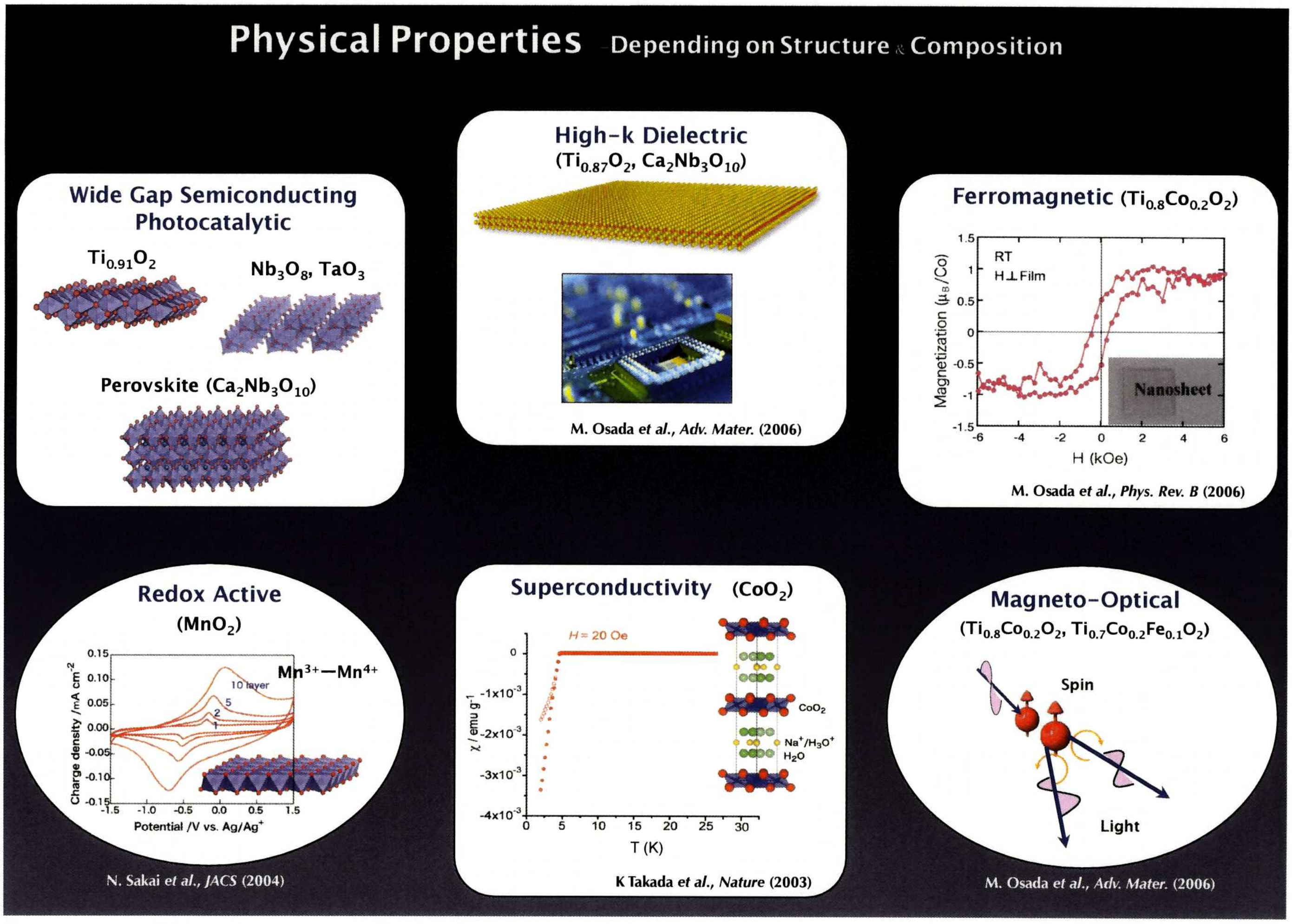
Nanosheet Process "Molecular Beaker Epitaxy"

Outline

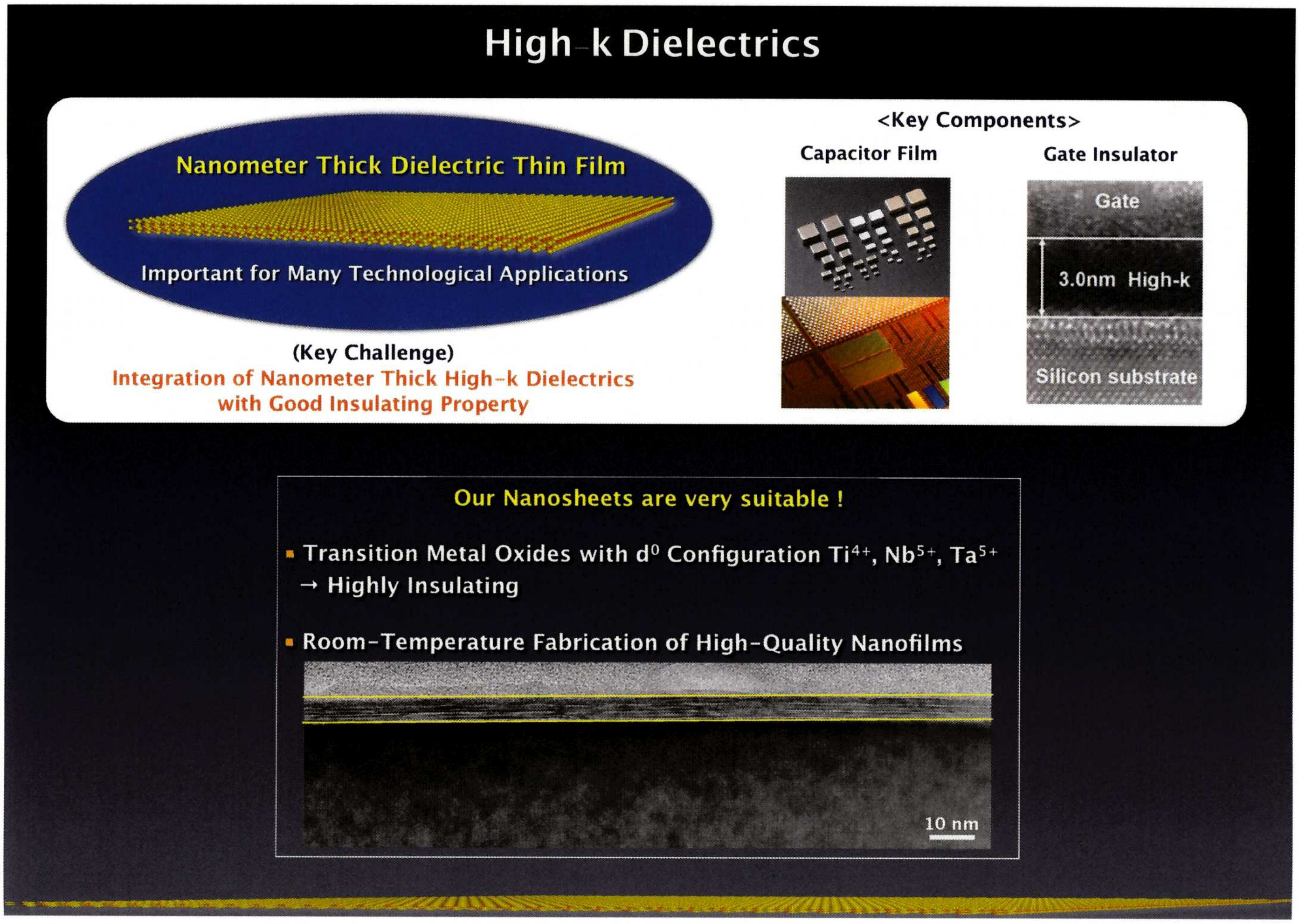
1. What is Oxide Nanosheet?

2. Materials Synthesis Using Oxide Nanosheets

3. Application to Nanoelectronics



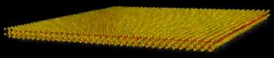
Physical Properties Depending on Structure & Composition
High-k Dielectric
($Ti_{0.87}O_2$, $Ca_2Nb_3O_{10}$)
M. Osada et al., Adv. Mater. (2006)
Wide Gap Semiconducting
Photocatalytic
$Ti_{0.91}O_2$
Nb_3O_8, TaO_3
Perovskite ($Ca_2Nb_3O_{10}$)
Ferromagnetic ($Ti_{0.8}Co_{0.2}O_2$)
RT
H⊥Film
Magnetization (μ_B/Co)
H (kOe)
Nanosheet
M. Osada et al., Phys. Rev. B (2006)
Redox Active
(MnO_2)
Mn^{3+}—Mn^{4+}
10 layer
Charge density /mA cm^{-2}
Potential /V vs. Ag/Ag$^+$
N. Sakai et al., JACS (2004)
Superconductivity (CoO_2)
H = 20 Oe
χ / emu g^{-1}
T (K)
CoO_2
Na^+/H_3O^+
H_2O
K Takada et al., Nature (2003)
Magneto-Optical
($Ti_{0.8}Co_{0.2}O_2$, $Ti_{0.7}Co_{0.2}Fe_{0.1}O_2$)
Spin
Light
M. Osada et al., Adv. Mater. (2006)

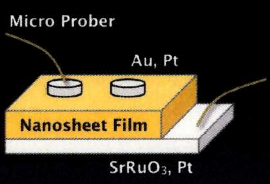


High-k Dielectrics
Nanometer Thick Dielectric Thin Film
Important for Many Technological Applications
(Key Challenge)
Integration of Nanometer Thick High-k Dielectrics
with Good Insulating Property
<Key Components>
Capacitor Film
Gate Insulator
Gate
3.0nm High-k
Silicon substrate
Our Nanosheets are very suitable !
Transition Metal Oxides with d^0 Configuration Ti^{4+}, Nb^{5+}, Ta^{5+}
→ Highly Insulating
Room-Temperature Fabrication of High-Quality Nanofilms
10 nm

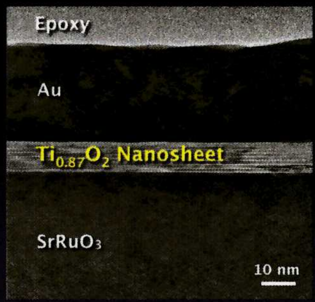
High-k Dielectric Nanosheets

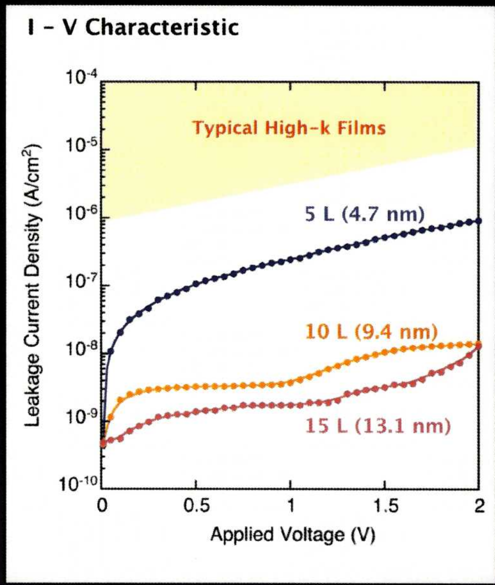
$Ti_{0.87}O_2$ Nanosheet





Nanocapacitor
- Au/(Nanosheet)$_n$/SrRuO$_3$
- Pt/(Nanosheet)$_n$/Pt



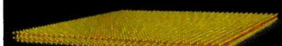


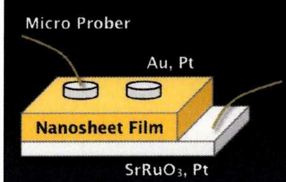
- Insulating Property Persists Even in Nanometer Thickness
-

M. Osada *et al.*, *Adv. Mater.* **18**, 1023 (2006); *ACS Nano* **3**, 1093 (2009)

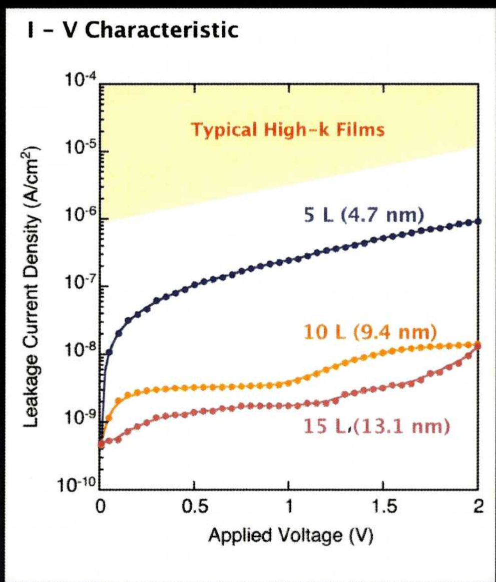
High-k Dielectric Nanosheets

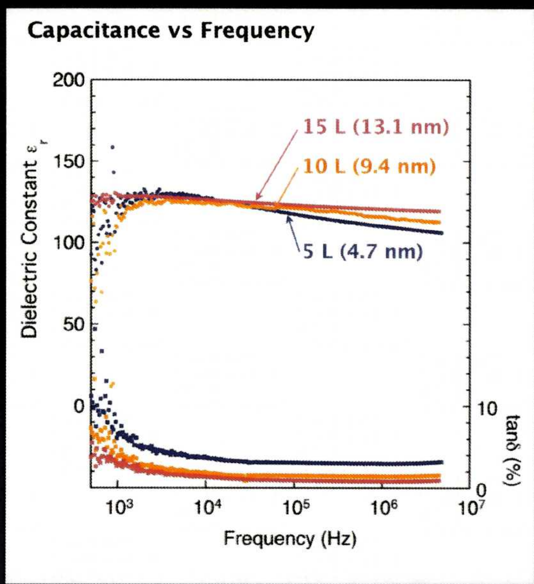
$Ti_{0.87}O_2$ Nanosheet





Nanocapacitor
- Au/(Nanosheet)$_n$/SrRuO$_3$
- Pt/(Nanosheet)$_n$/Pt





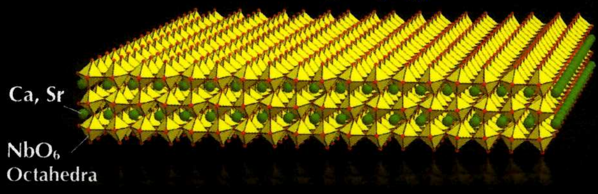
- Insulating Property Persists Even in Nanometer Thickness
- High Dielectric Constant Exceeding 100

  - Useful for Practical Applications-

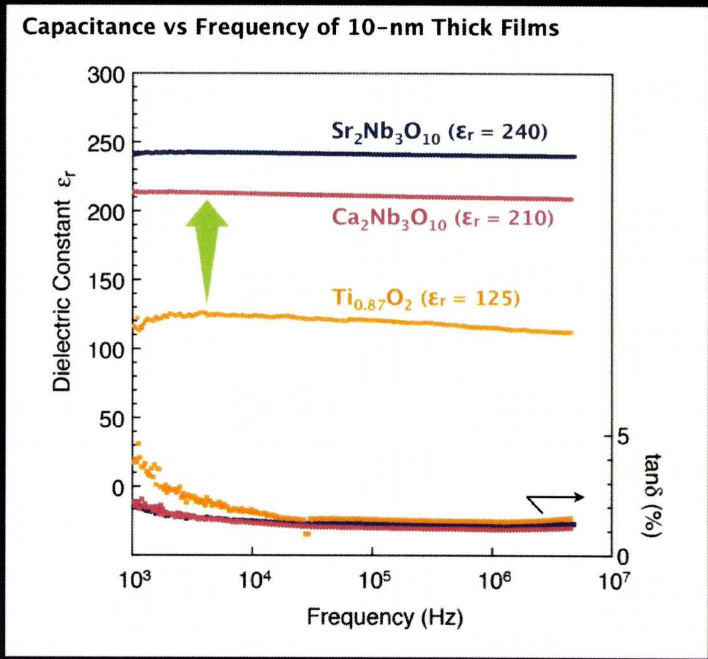
M. Osada *et al.*, *Adv. Mater.* **18**, 1023 (2006); *ACS Nano* **3**, 1093 (2009)

High-k Perovskite Nanosheets

$(Ca,Sr)_2Nb_3O_{10}$



Nanosheets with 3 Octahedral Units

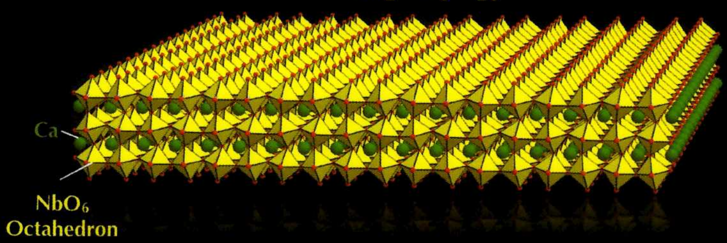


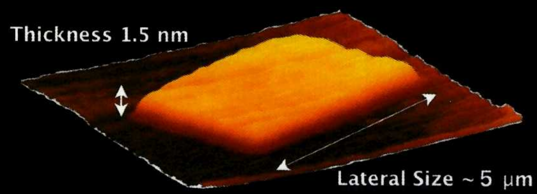
Enhanced k Value (210~240) in Perovskite Nanosheets

M. Osada *et al.*, *ACS Nano* **4**, 5225 (2010)

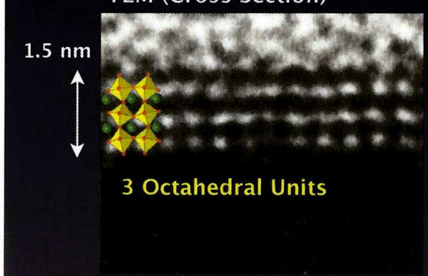
High-k Perovskite Nanosheets

$Ca_2Nb_3O_{10}$

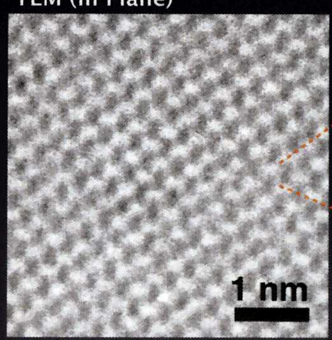


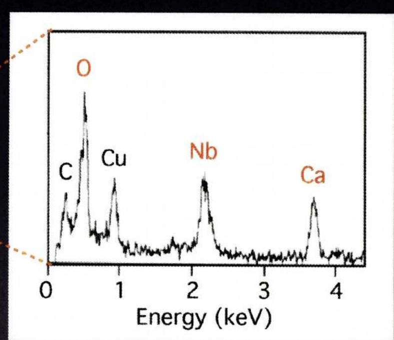


TEM (Cross Section)

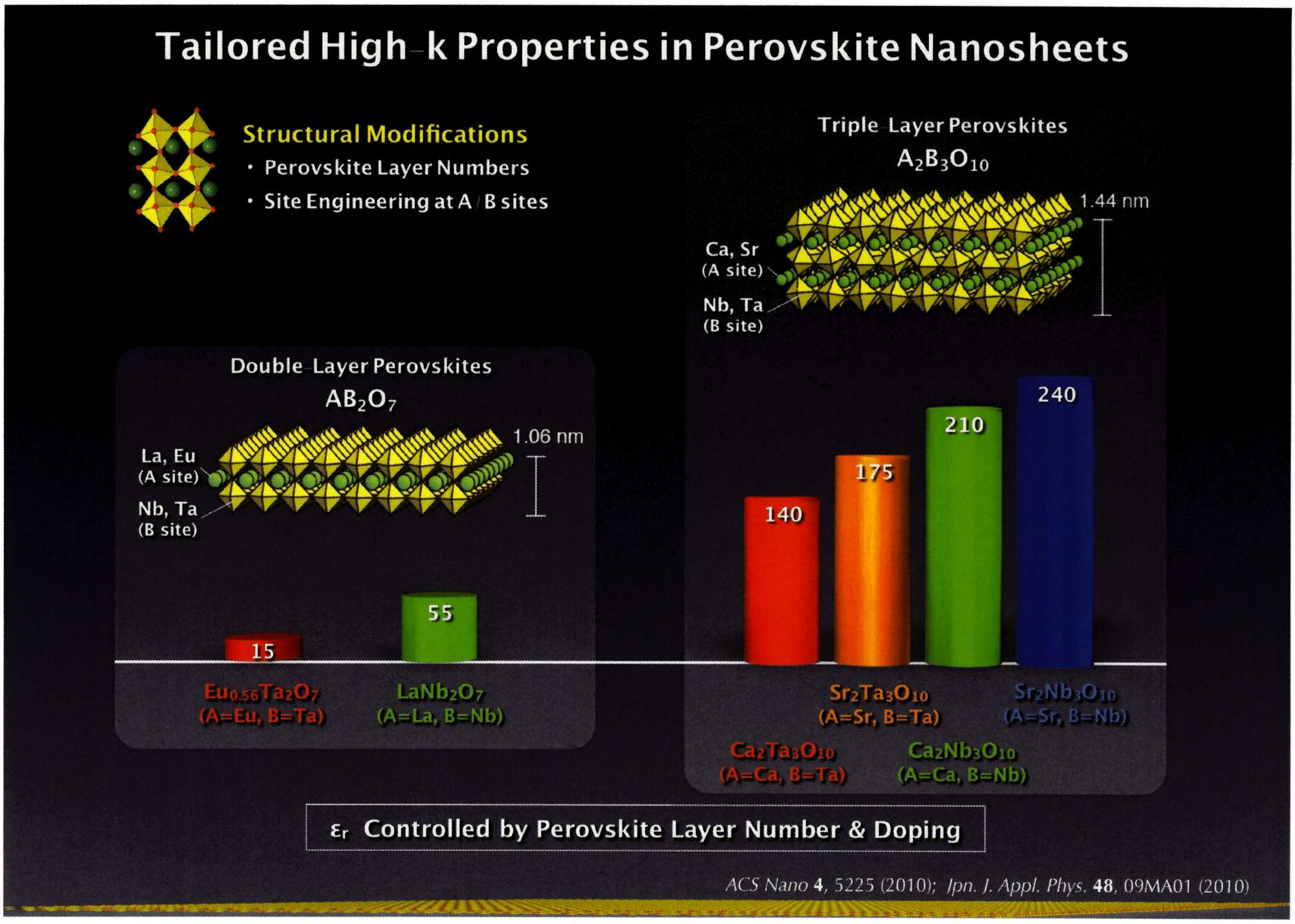


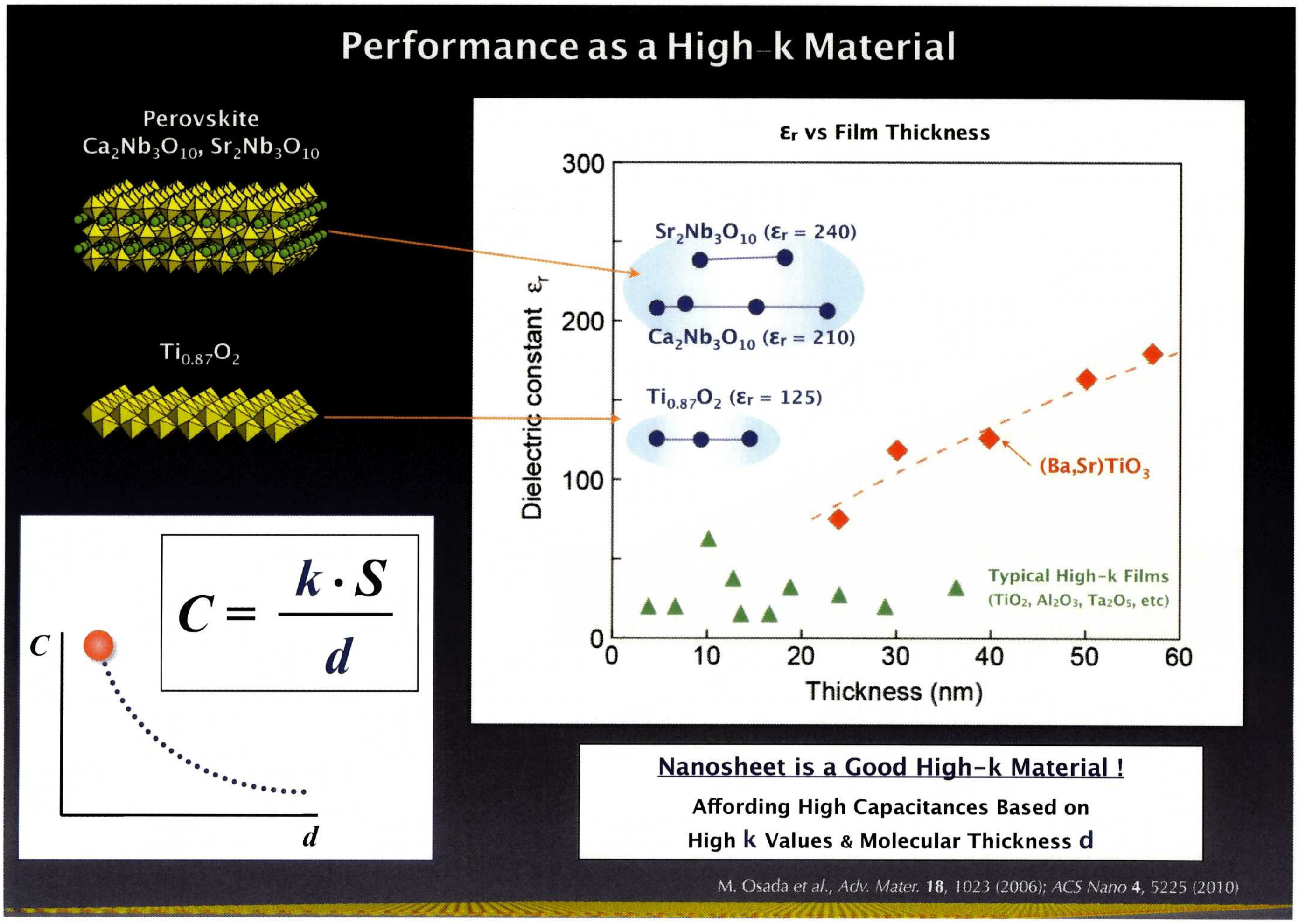
TEM (In Plane)

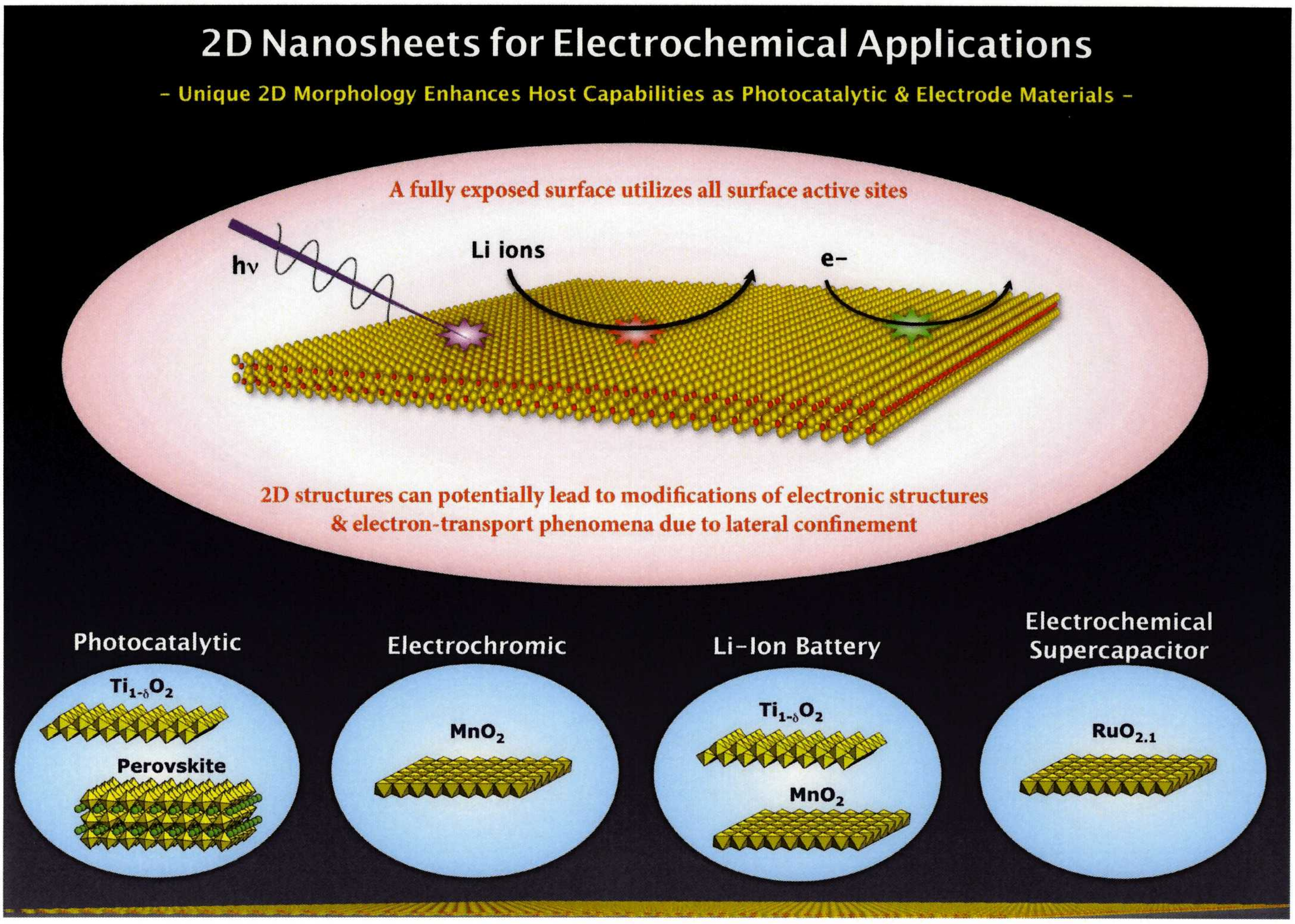


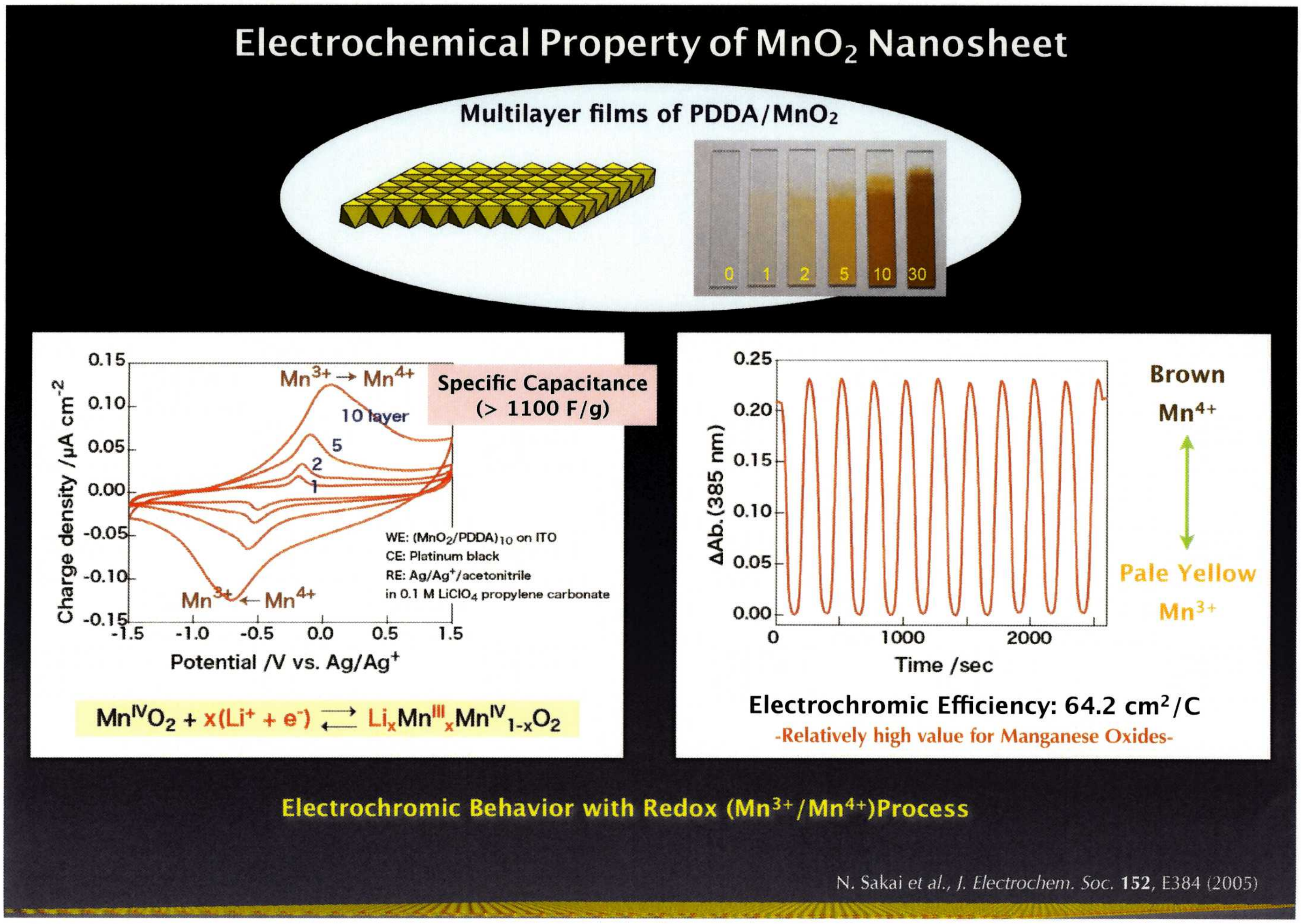


Ideal High-k Perovskite Film with Critical Thickness


Tailored High-k Properties in Perovskite Nanosheets
Structural Modifications
• Perovskite Layer Numbers
• Site Engineering at A/B sites
Triple-Layer Perovskites
$A_2B_3O_{10}$
1.44 nm
Ca, Sr
(A site)
Nb, Ta
(B site)
Double-Layer Perovskites
AB_2O_7
La, Eu
(A site)
Nb, Ta
(B site)
1.06 nm
15
55
140
175
210
240
$Eu_{0.56}Ta_2O_7$ (A=Eu, B=Ta)
$LaNb_2O_7$ (A=La, B=Nb)
$Ca_2Ta_3O_{10}$ (A=Ca, B=Ta)
$Sr_2Ta_3O_{10}$ (A=Sr, B=Ta)
$Ca_2Nb_3O_{10}$ (A=Ca, B=Nb)
$Sr_2Nb_3O_{10}$ (A=Sr, B=Nb)
ε_r Controlled by Perovskite Layer Number & Doping
ACS Nano 4, 5225 (2010); Jpn. J. Appl. Phys. 48, 09MA01 (2010)

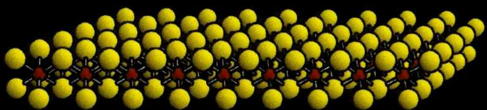

Performance as a High-k Material
Perovskite
$Ca_2Nb_3O_{10}$, $Sr_2Nb_3O_{10}$
$Ti_{0.87}O_2$
ε_r vs Film Thickness
$Sr_2Nb_3O_{10}$ (ε_r = 240)
$Ca_2Nb_3O_{10}$ (ε_r = 210)
$Ti_{0.87}O_2$ (ε_r = 125)
(Ba,Sr)TiO_3
Typical High-k Films
(TiO_2, Al_2O_3, Ta_2O_5, etc)
Dielectric constant ε_r
Thickness (nm)
0
10
20
30
40
50
60
100
200
300
$C = \frac{k \cdot S}{d}$
C
d
Nanosheet is a Good High-k Material !
Affording High Capacitances Based on
High k Values & Molecular Thickness d
M. Osada et al., Adv. Mater. 18, 1023 (2006); ACS Nano 4, 5225 (2010)


2D Nanosheets for Electrochemical Applications
- Unique 2D Morphology Enhances Host Capabilities as Photocatalytic & Electrode Materials -
A fully exposed surface utilizes all surface active sites
hν
Li ions
e−
2D structures can potentially lead to modifications of electronic structures
& electron-transport phenomena due to lateral confinement
Photocatalytic
$Ti_{1-δ}O_2$
Perovskite
Electrochromic
MnO_2
Li-Ion Battery
$Ti_{1-δ}O_2$
MnO_2
Electrochemical Supercapacitor
$RuO_{2.1}$


Electrochemical Property of MnO_2 Nanosheet
Multilayer films of PDDA/MnO_2
0 1 2 5 10 30
$Mn^{3+} \rightarrow Mn^{4+}$
Specific Capacitance (> 1100 F/g)
10 layer
5
2
1
Charge density /μA cm^{-2}
Potential /V vs. Ag/Ag$^+$
WE: $(MnO_2/PDDA)_{10}$ on ITO
CE: Platinum black
RE: Ag/Ag$^+$/acetonitrile
in 0.1 M $LiClO_4$ propylene carbonate
$Mn^{3+} \leftarrow Mn^{4+}$
$Mn^{IV}O_2 + x(Li^+ + e^-) \rightleftarrows Li_xMn^{III}_xMn^{IV}_{1-x}O_2$
ΔAb.(385 nm)
Time /sec
Brown
Mn^{4+}
Pale Yellow
Mn^{3+}
Electrochromic Efficiency: 64.2 cm^2/C
-Relatively high value for Manganese Oxides-
Electrochromic Behavior with Redox (Mn^{3+}/Mn^{4+}) Process
N. Sakai et al., J. Electrochem. Soc. 152, E384 (2005)

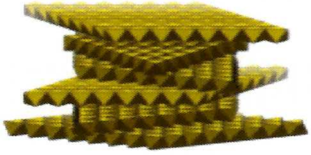
New Layered $LiMnO_2$ for Li-Ion Battery

MnO_2 Nanosheet



Flocculation
by mixing with LiOH

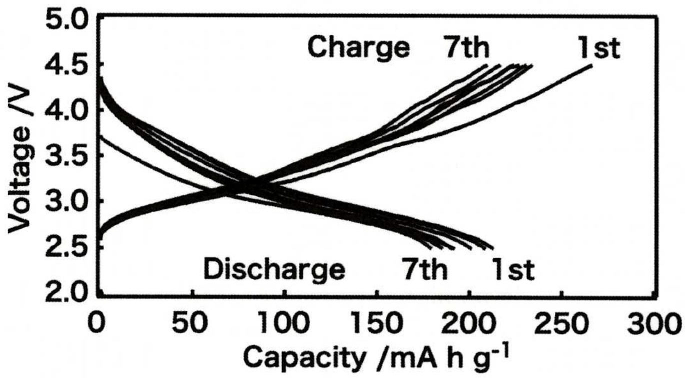
New Layered Form
$Li_{0.36}MnO_2 \cdot 0.7H_2O$



Turbostratically Stacked
Nanosheets

Layered $LiMnO_2$

Cheap & Environmentally Benign Electrode Material
A Candidate to Replace of $LiCoO_2$
Suffers from Degradation due to Spinel Formation

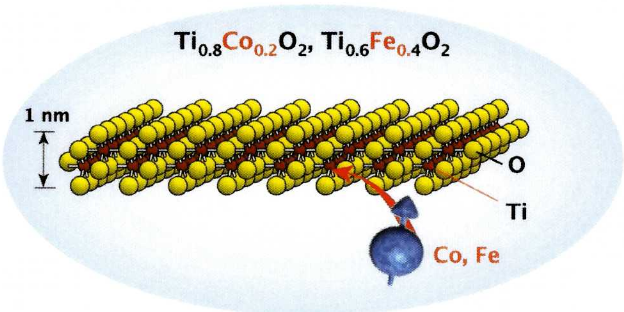


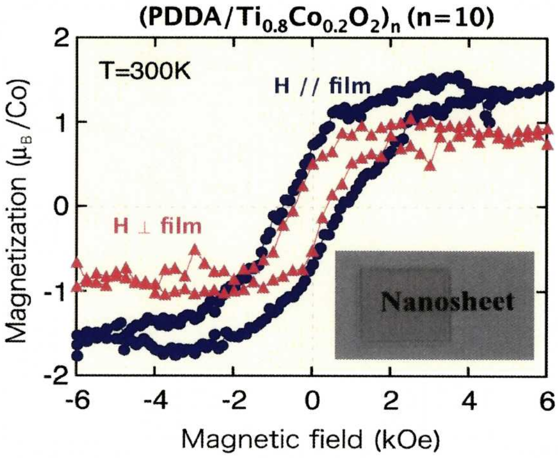
Nanosheet-Derived $LiMnO_2$ Retains Large Capacity (79 mAh/g),
Eliminating Degradation Problems due to Spinel Formation

L. Wang *et al.*, *Chem. Mater.* **15**, 4508 (2003)

Ferromagnetic Nanosheets

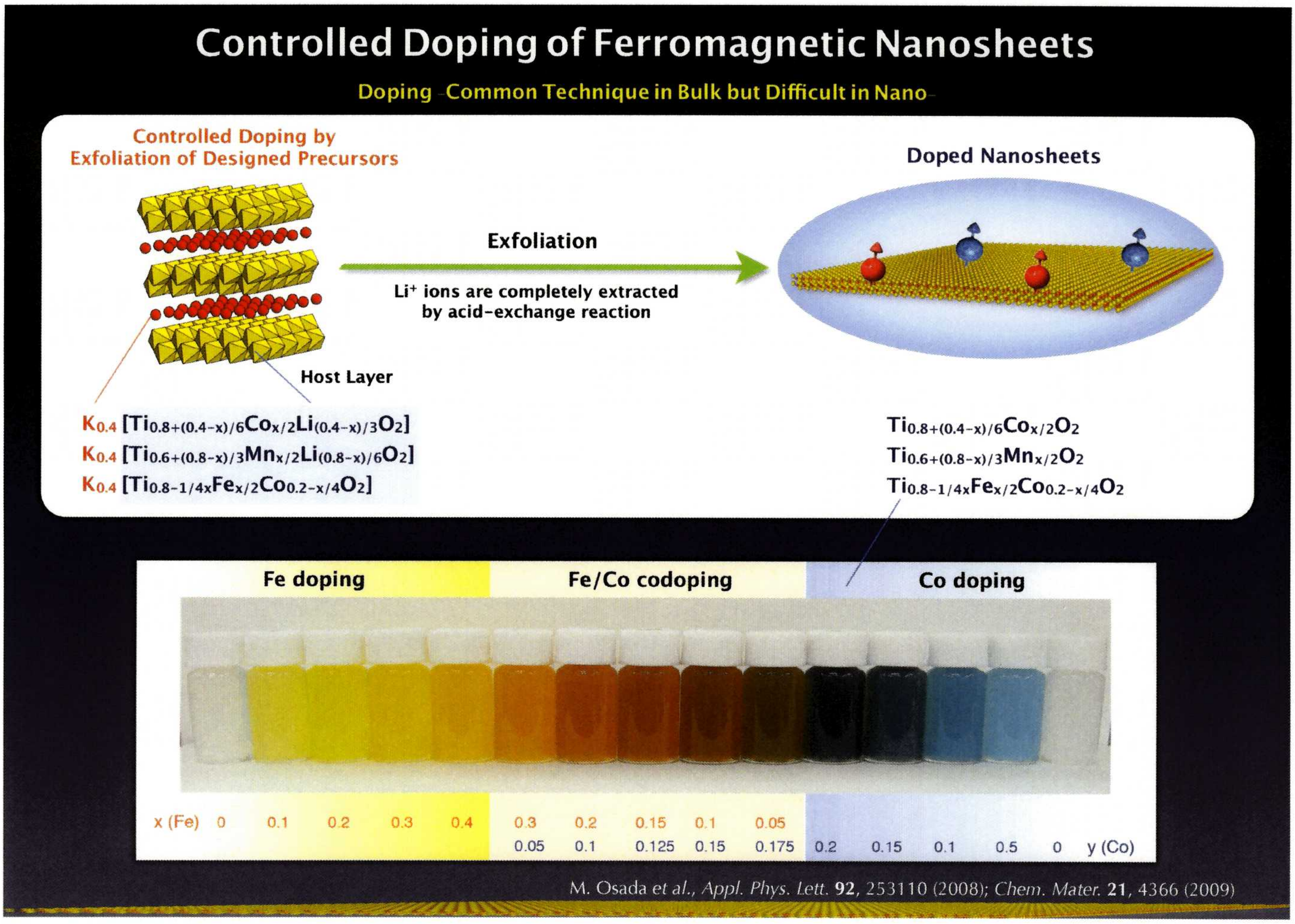
Co, Fe-Substituted TiO_2 Nanosheet

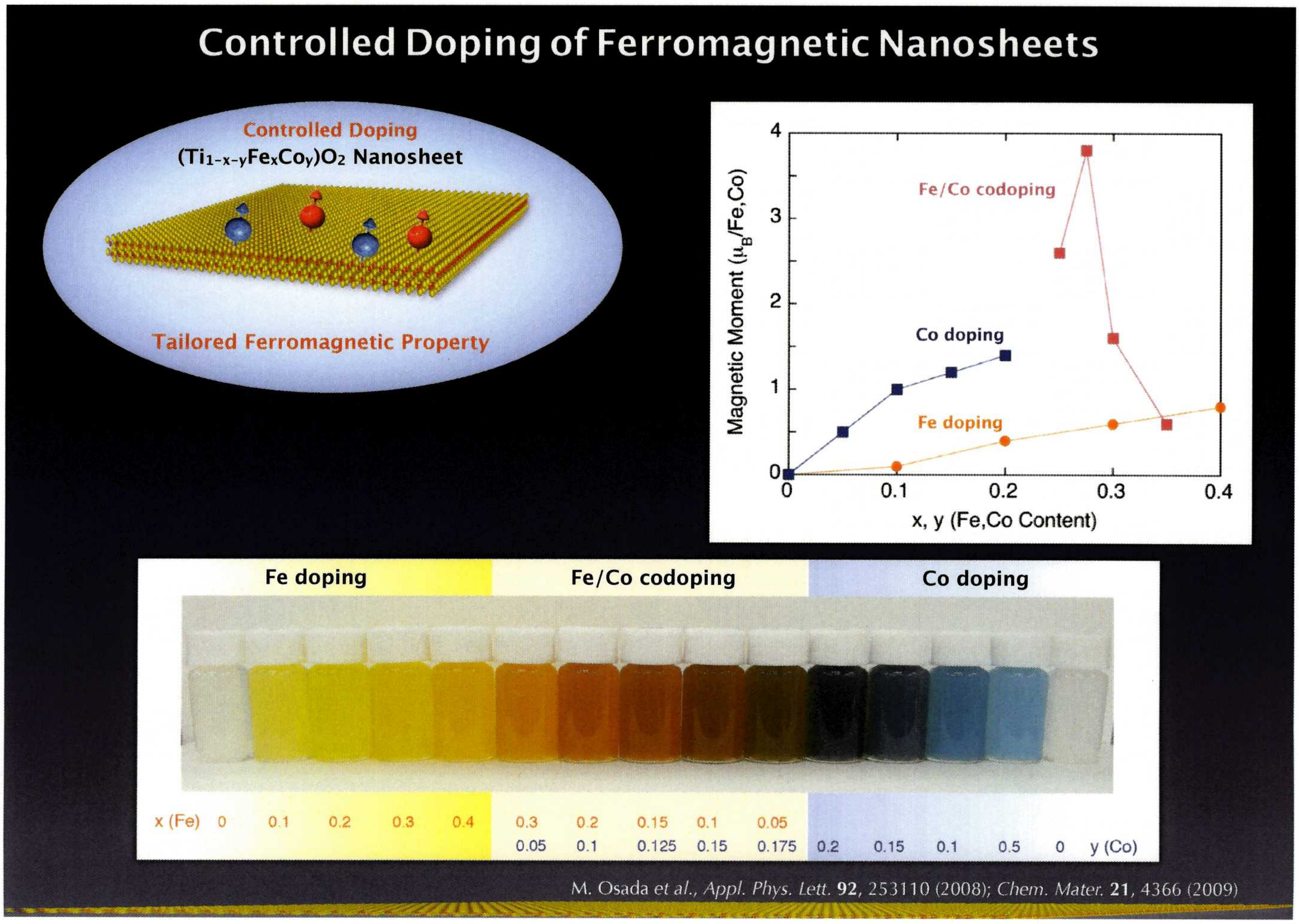


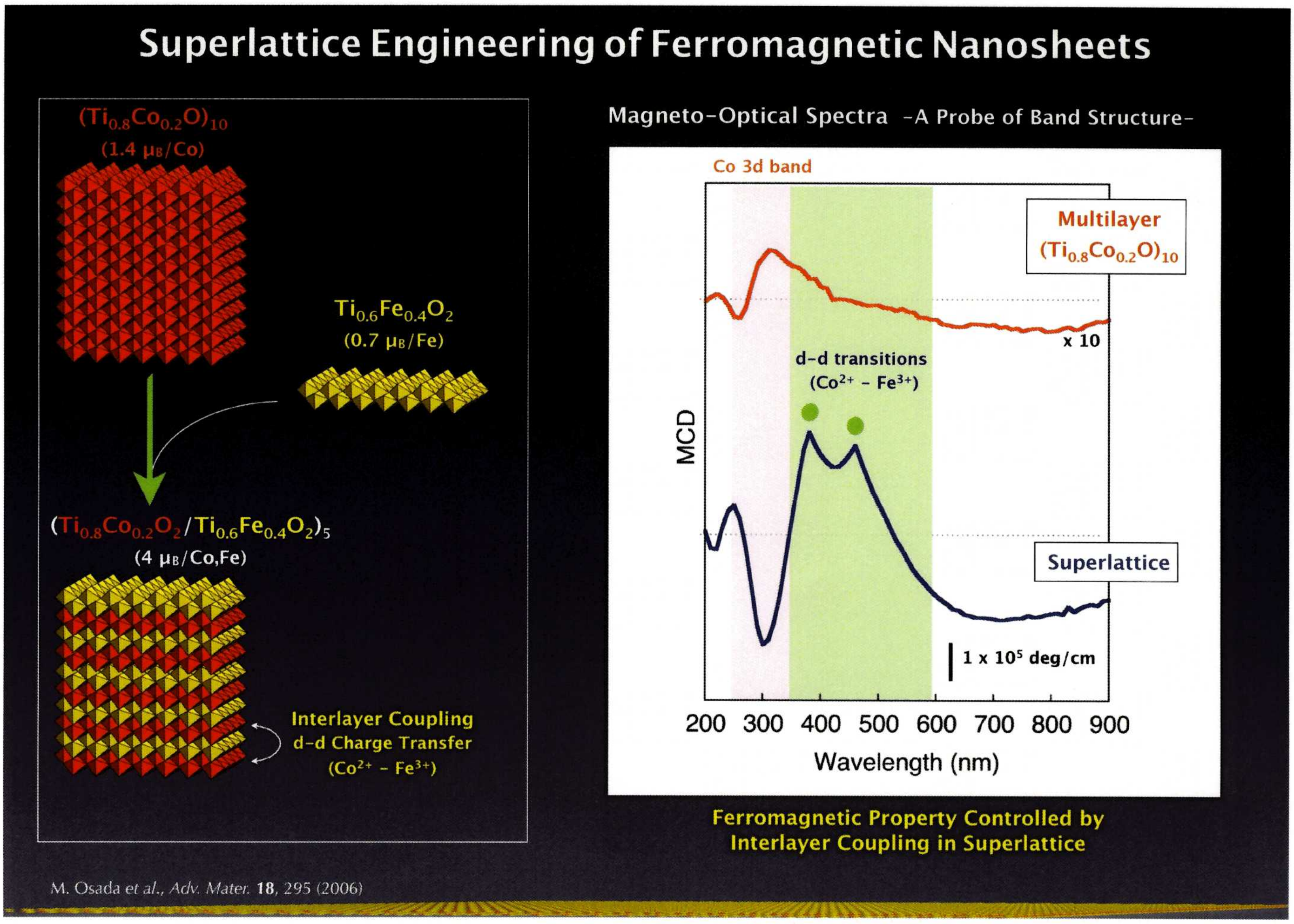


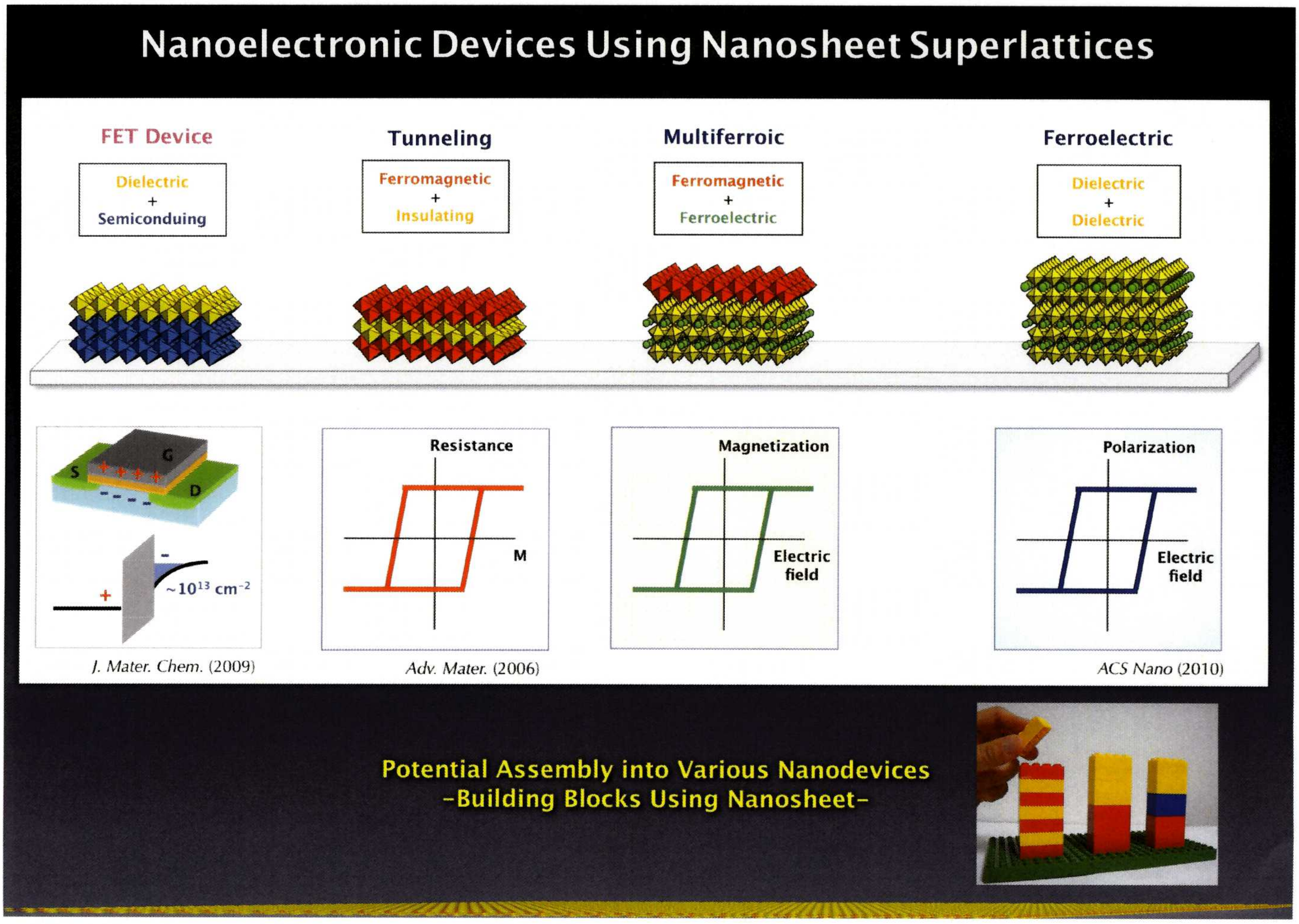
RT Ferromagnetism	**Comparative to Co-doped Anatase** Y. Matsumoto et al., Science 291, 854 (2001)
Wide Gap	**MO Response in UV Light**
Controlled Doping	**Tailored Ferromagnetic Property**
LBL Assembly	**Superlattice Approach**

M. Osada *et al.*, *Adv. Mater.* **18**, 295 (2006); *Phys. Rev. B* **73**, 153301 (2006)


Controlled Doping of Ferromagnetic Nanosheets
Doping -Common Technique in Bulk but Difficult in Nano-
Controlled Doping by
Exfoliation of Designed Precursors
Doped Nanosheets
Exfoliation
Li^+ ions are completely extracted
by acid-exchange reaction
Host Layer
$K_{0.4}$ [$Ti_{0.8+(0.4-x)/6}Co_{x/2}Li_{(0.4-x)/3}O_2$]
$K_{0.4}$ [$Ti_{0.6+(0.8-x)/3}Mn_{x/2}Li_{(0.8-x)/6}O_2$]
$K_{0.4}$ [$Ti_{0.8-1/4x}Fe_{x/2}Co_{0.2-x/4}O_2$]
$Ti_{0.8+(0.4-x)/6}Co_{x/2}O_2$
$Ti_{0.6+(0.8-x)/3}Mn_{x/2}O_2$
$Ti_{0.8-1/4x}Fe_{x/2}Co_{0.2-x/4}O_2$
Fe doping
Fe/Co codoping
Co doping
x (Fe) 0 0.1 0.2 0.3 0.4 0.3 0.2 0.15 0.1 0.05
0.05 0.1 0.125 0.15 0.175 0.2 0.15 0.1 0.5 0 y (Co)
M. Osada et al., Appl. Phys. Lett. 92, 253110 (2008); Chem. Mater. 21, 4366 (2009)

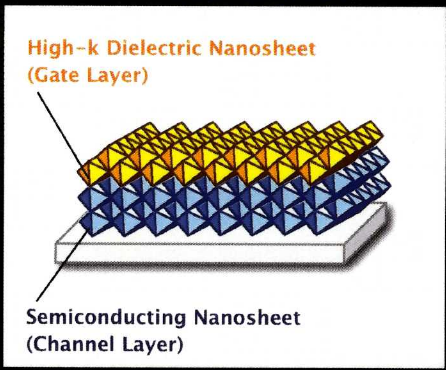

Controlled Doping of Ferromagnetic Nanosheets
Controlled Doping
($Ti_{1-x-y}Fe_xCo_y$)O_2 Nanosheet
Tailored Ferromagnetic Property
Magnetic Moment (μ_B/Fe,Co)
x, y (Fe,Co Content)
0 0.1 0.2 0.3 0.4
0 1 2 3 4
Fe/Co codoping
Co doping
Fe doping
Fe doping
Fe/Co codoping
Co doping
x (Fe) 0 0.1 0.2 0.3 0.4 0.3 0.2 0.15 0.1 0.05
0.05 0.1 0.125 0.15 0.175 0.2 0.15 0.1 0.5 0 y (Co)
M. Osada et al., Appl. Phys. Lett. 92, 253110 (2008); Chem. Mater. 21, 4366 (2009)

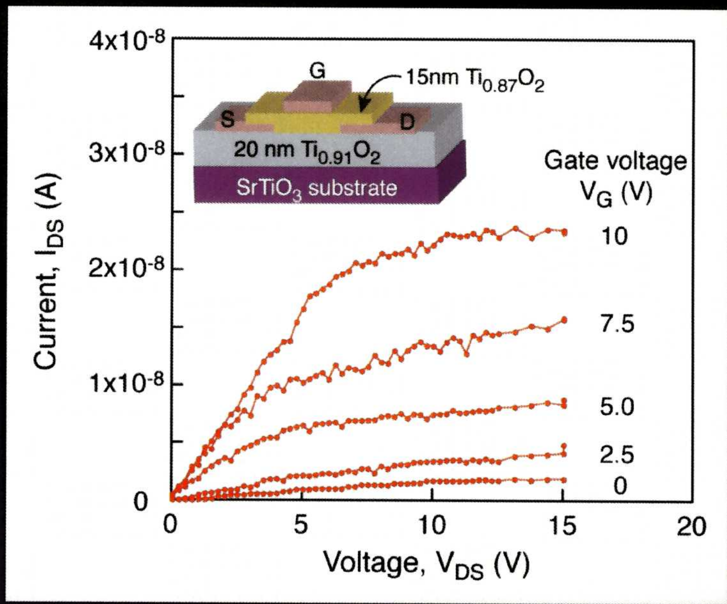

Superlattice Engineering of Ferromagnetic Nanosheets
(Ti0.8Co0.2O)10
(1.4 μB/Co)
Ti0.6Fe0.4O2
(0.7 μB/Fe)
(Ti0.8Co0.2O2/Ti0.6Fe0.4O2)5
(4 μB/Co,Fe)
Interlayer Coupling
d-d Charge Transfer
(Co2+ - Fe3+)
Magneto-Optical Spectra -A Probe of Band Structure-
Co 3d band
Multilayer
(Ti0.8Co0.2O)10
x 10
d-d transitions
(Co2+ - Fe3+)
MCD
Superlattice
1 x 10^5 deg/cm
200 300 400 500 600 700 800 900
Wavelength (nm)
Ferromagnetic Property Controlled by
Interlayer Coupling in Superlattice
M. Osada et al., Adv. Mater. 18, 295 (2006)


Nanoelectronic Devices Using Nanosheet Superlattices
FET Device
Dielectric
+
Semiconduing
Tunneling
Ferromagnetic
+
Insulating
Multiferroic
Ferromagnetic
+
Ferroelectric
Ferroelectric
Dielectric
+
Dielectric
S
G
D
~10^13 cm^-2
Resistance
M
Magnetization
Electric field
Polarization
Electric field
J. Mater. Chem. (2009)
Adv. Mater. (2006)
ACS Nano (2010)
Potential Assembly into Various Nanodevices
-Building Blocks Using Nanosheet-

All Nanosheet FET Device

Self Assembled FET





- Accumulation Mode with Mobility of 5 x 10^2 cm^2/Vs
- ON/OFF Current Ratio of 10^3

A Step Towards Self-Assembled Nanodevices Using Nanosheets

M. Osada & T. Sasaki, *J. Mater. Chem.* (2009)

Summary

We present some unique aspects of nanosheets, particular focusing on a bottom-up fabrication for functional thin films using oxide nanosheets as a building block.

Functional oxide nanosheets was synthesized by delaminating appropriate layered precursors, which show attractive physical and chemical properties.

Nanosheets were self-assembled via various soft-chemistry processes to produce a range of nanostructured films, in which architectures can be precisely controlled.

The careful placements of functional oxide nanosheets into film architectures allow the rational design of advanced functional devices, including high-k nanofilm, ferroelectric memory, Li battery, RT ferromagnet, magneto-optical device, FET, etc.