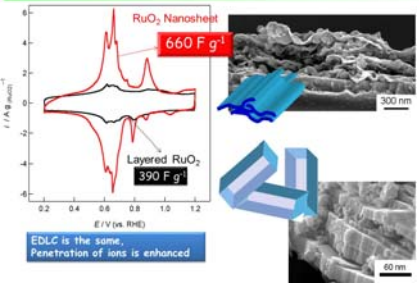
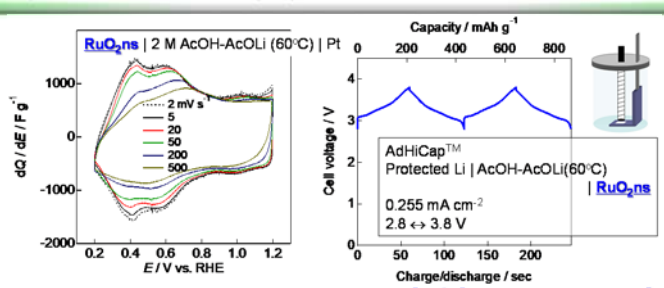
Conducting Nanosheets
- New Frontier in Next-Generation Supercapacitors and Fuel Cell Electrocatalysts -

Center for Energy and Environmental Science
X-Breed
信州大学 SHINSHU UNIVERSITY
Faculty of Textile Science and Technology

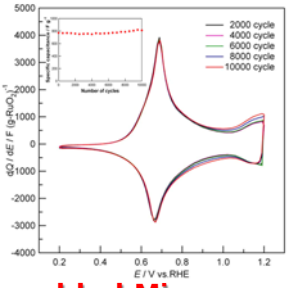
High capacitance, long cycle life and high power pseudopcapacitors
Supercapacitor application of nanosheets

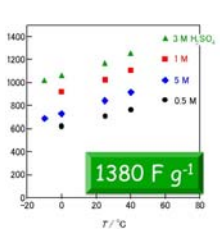


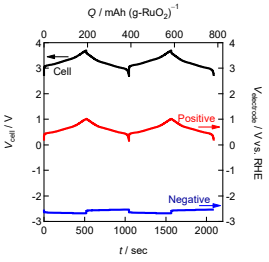


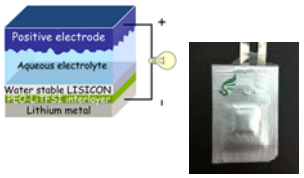
- Nanosheets outperform their nanoparticle analogue, affording high pseudo-capacitance (~1000 F/g; 5-10 times higher than typical porous carbons) in H_2SO_4.
- Buffered solutions (acetic acid-lithium acetate) can also be used as a benign electrolyte.
- The pseudocapacitive nanosheets can be used as the positive electrode with aqueous electrolytes in combination with a protected Li or Li-doped carbon anode for 4-V rated advanced hybrid supercapacitors (AdHiCap™).
- AdHiCap™ shows performance that can compete with present Lithium-ion battery technology.

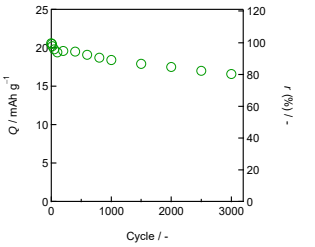
4-V Aqueous Hybrid Supercaps (AdHiCap™)





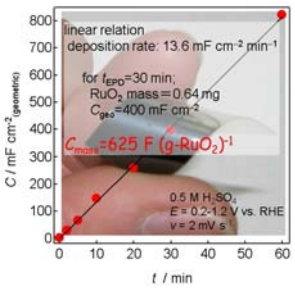


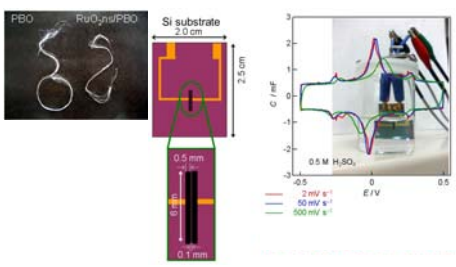


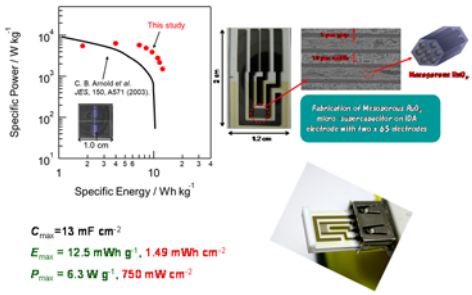


- 920 F $(g\text{-}RuO_2)^{-1}$ [196 mAh $(g\text{-}RuO_2)^{-1}$]
- 625 Wh $(kg\text{-}RuO_2)^{-1}$

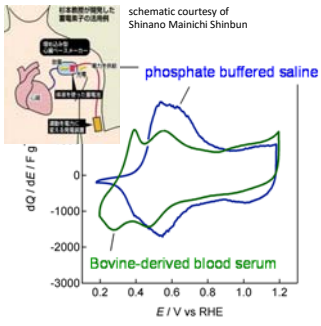
Value-added Micro-supercaps, Flexible-supercaps, Bio-supercaps







Cmax=13 mF cm-2
Emax = 12.5 mWh g-1, 1.49 mWh cm-2
Pmax = 6.3 W g-1, 750 mW cm-2



- Nanosheets can be used for various valued-added devices including, Micro-supercaps, super-flexible supercaps, and Bio-supercaps.
- Minro-supercaps and nanosheet coated-fibers will allow realization of wearable electronics.
- RuO_2 nanosheets can be used in bio-electrolytes such as PBS and blood serum, allowing safe implantable energy storage.

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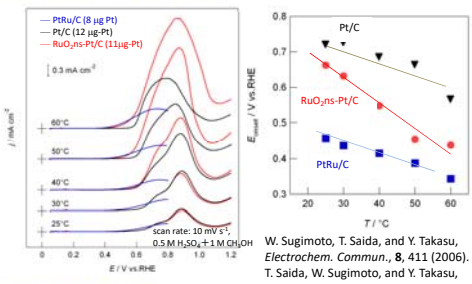
High surface area and durable electrocatalysts and co-catalysts
Electrocatalysts for Fuel Cells and Electrolyzers

Nanosheet Fuel Cell Co-Catalysts

Methanol oxidation (MOR)



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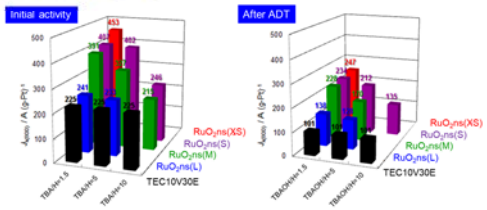
T. Saida, W. Sugimoto, and Y. Takasu, *Electrochim. Acta*, **55**, 857 (2010).

O_2 reduction (ORR)



D. Takimoto, C. Chauvin, and W. Sugimoto, *Electrochem. Commun.*, **33**, 123 (2013).
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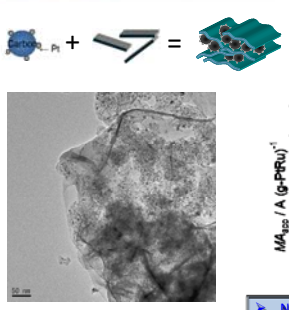
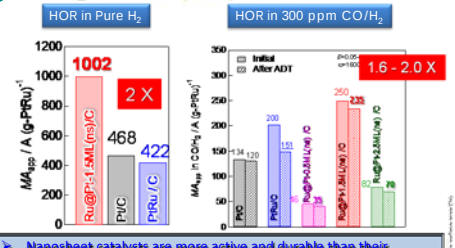


- Addition of RuO_2ns to Pt/C enhances electrooxidation of CO and CH_3OH.
- Addition of RuO_2ns to Pt/C enhances electroreduction of O_2 (ORR) by 2 times.
- RuO_2ns acts as co-catalyst above 40°C and shows comparable performance to PtRu alloys
- RuO_2ns is more stable than Ru metal, and thus RuO_2ns-Pt/C is more durable than Pt/C and PtRu/C.

Metallic Ru@Pt core-shell nanosheets

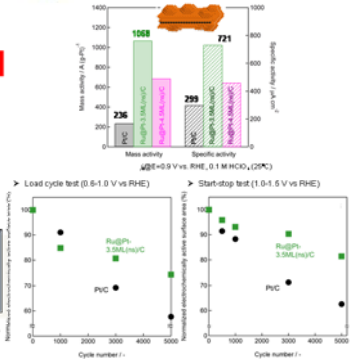
H_2 oxidation (HOR)



- Nanosheet catalysts are more active and durable than their nanoparticle analogues.
- Can be used for both anode and cathode.
- Possible 90% reduction of Pt usage.

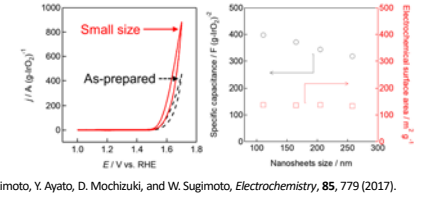
D. Takimoto, T. Ohnishi, J. Nutariya, Z. Shen, Y. Ayato, D. Mochizuki, A. Demortière, A. Boulineau, W. Sugimoto, *J. Catal.*, **345**, 207 (2017).

O_2 reduction (ORR)



IrO_2 Nanosheets

- IrO_2ns are highly active for Oxygen reduction reaction (OER)
- Edge are the active sites



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Acknowledgements

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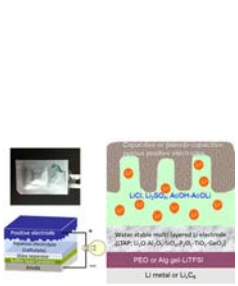
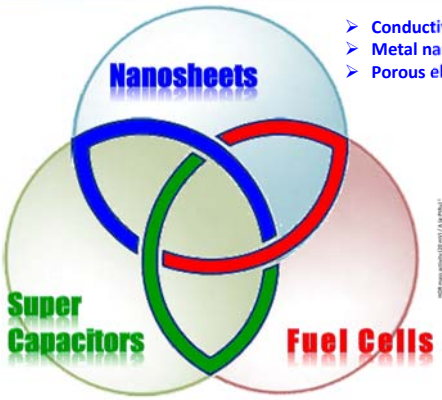
Who we are and what we do

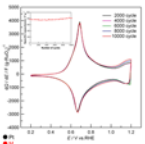
Energy materials for storage and conversion

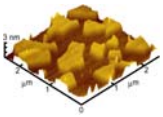


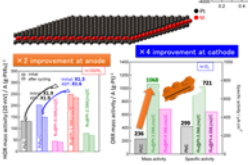
- Pseudocapacitive materials
- Charge storage mechanism
- Value-added devices
- Hybrid devices



- Conductive oxide nanosheets
- Metal nanosheet catalysts
- Porous electrode fabrication





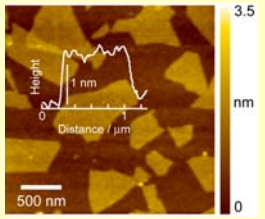


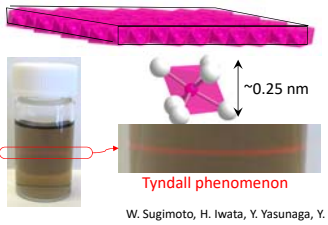
- Nanostructured Pt and Pt alloys, core-shell structures
- Model electrode studies and kinetics
- Pt-free catalysts

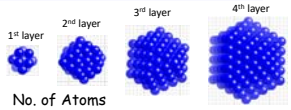
Nanosheet
1 nm thick 2D crystallites

Characteristics
- "All surface"
- Anisotropic single crystalline colloid
- Stiff & Flexible
- Ionic & Covalent bonds
- Cluster/molelular size
- Surface Functionality
- Diversity in composition
- Distinic "Site Engineering"

⇒ Designer Material
⇒ Nano Building Block (Nano-LEGO) for 3-D architecture





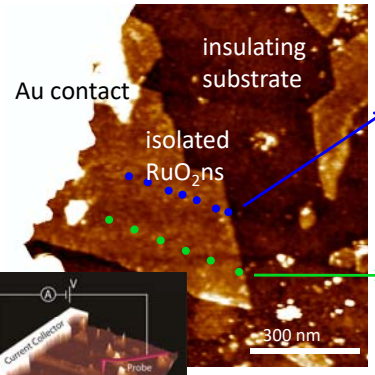


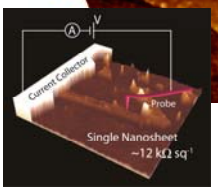
<Dimensional Control of Nanomaterials>
1D → Nanowire, Nanotube, Nanofiber
2D → Nanosheet
3D → Bulk

Shinshu Univ. original RuO_2 and IrO_2 nanosheets

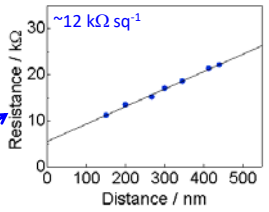
- ✓ $Ru^{4+}O_2$ nanosheet derived from layered $K_{0.2}RuO_{2.1}$
- ✓ $Ru^{3.8+}O_2$ nanosheet derived from layered α-$NaFeO_2$-type $Na_{0.2}RuO_2$
- ✓ IrO_2 nanosheet derived from layered $K_xIr_yO_z$

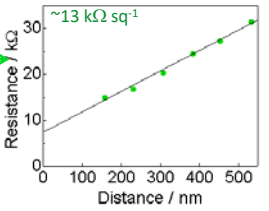
A typical nanosheet colloid





Conductivity of single nanosheet





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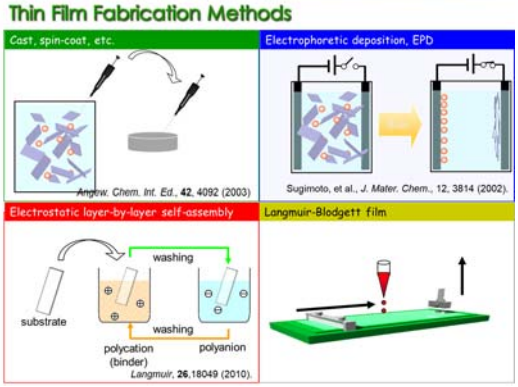
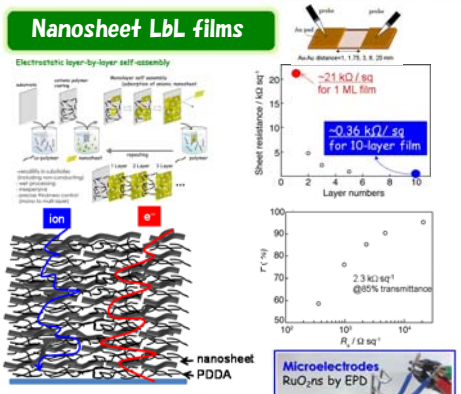
Wet processing techniques for nm to μm thick nanosheet electrodes

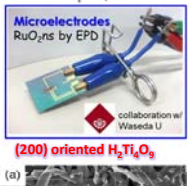
Layer-by-Layer Deposition, Electrophoretic Deposition

Thin Film Fabrication Methods



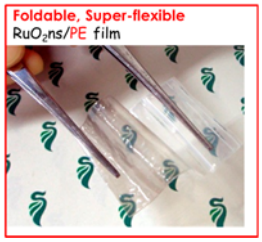
Nanosheet LbL films



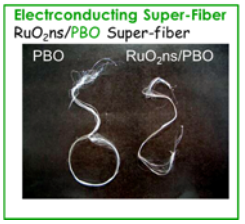


Bendable& Corrosion Resistant RuO_2ns/PET

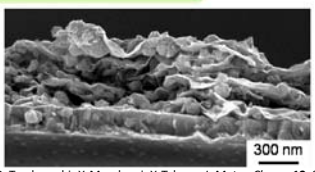
Foldable, Super-flexible RuO_2ns/PE film



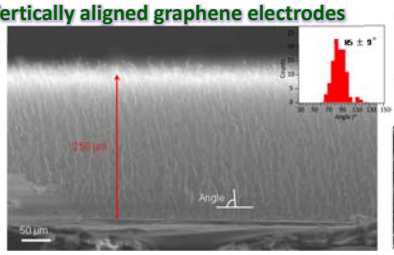
Electrconducting Super-Fiber RuO_2ns/PBO Super-fiber



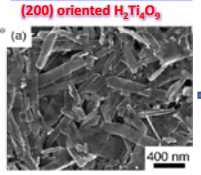
Nanosheet EPD films



Vertically aligned graphene electrodes

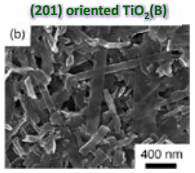


(200) oriented $H_2Ti_4O_9$



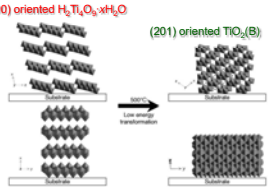
500℃

(201) oriented TiO_2(B)



(200) oriented $H_2Ti_4O_9 \cdot xH_2O$

(201) oriented TiO_2(B)



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