# Selected Novel Technologies for Licensing

# **MRS Fall 2011**

**Carbon Related Materials** 

 Graphene, Bucky Gel, Bucky Ball, Carbon Nanotube, Carbon Nanohorn, Carbon Nanowall etc.

# **Other Innovative Technologies**

 Isotopomer, Dendrimer, Optical Catalyst, 12CaO•7Al<sub>2</sub>O<sub>3</sub>, MRDFT etc.



Japan Science and Technology Agency

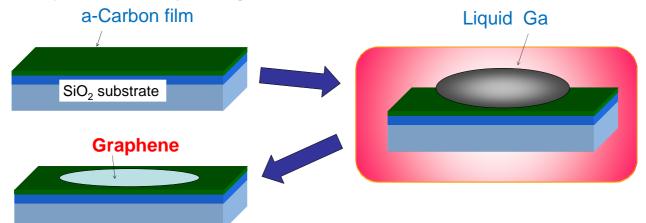
# Carbon Related **Materials** R

# Fabrication of Graphene Using Liquid Ga and its Electrical Properties

### **1. Fabrication of Graphene film**

### Prof. Jun-ichi FUJITA (University of Tsukuba)

- 20nm amorphous-Carbon film is deposited on the substrate.
- Liquid Ga is put on the amorphous carbon film and is annealed at 1000°C for 30 min under 5 x 10<sup>-4</sup>Pa.
- Ga droplet is removed by soaking it in dilute HCl.



(c).

10 nm

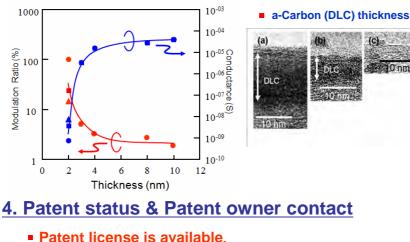
(b)

DEC

### 2. Feature of Our Method

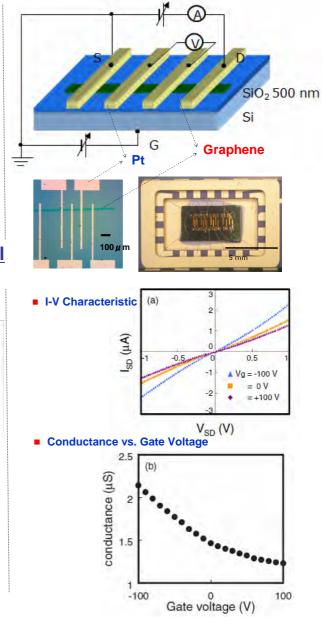
Method	Mechanical Delamination	High temperature anneal of carbon film on SiC crystal substrate	High temperature CVD on metal crystal substrate	Our method
Example	K. S. Novoselov et al. PNAS 102 (2005) 10451.	W. Norimatsu,et al.Chem. Phys. Lett. 488 (2009) 52. 21日 スローマングラー ストン・ 3年 ファー ファー	J. Coraux et al. Nano Lett. 8 (2008) 565.	J. Fujita et al. J. Appl. Phys. Lett. 49, 060C01 (2010)
Fabrication Temperature	-	1500 <b>°C</b>	900~1000° <b>C</b>	900~1000 <b>℃</b>
Large area fabrication	x	Δ	0	0
Electron mobility	0	0	0	Δ ( improved )
High volume production	XX	x	0	0
Device fabrication	x	Δ	0	0
Others		Expensive SiC crystal		•Flexible substrate is available •No transcription

### 4. a-Carbon Thickness Dependencies of Channel **Conductance and Moduration ratio**



Patent No. : PCT/JP2010/054602 Patent owner contact: Masaru OZAKI (JST) Tel:+81-3-5214-8486 e-mail: license@jst.go.jp

### 3. Trial of Graphene Transistor

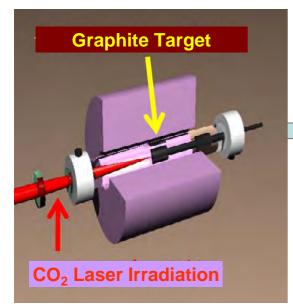


# **Carbon Nanohorn**

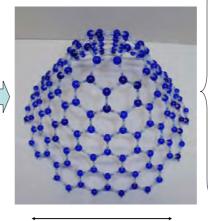
Prof. Sumio IIJIMA (Meijo University) Prof. emeritus Hidekazu TOUHARA (Shinshu University)

### **Fabrication of Carbon Nanohorn**

Carbon nanohorns are manufactured by the CO<sub>2</sub> laser ablation of carbon.



**Carbon Nanohorn** 



2~4 nm

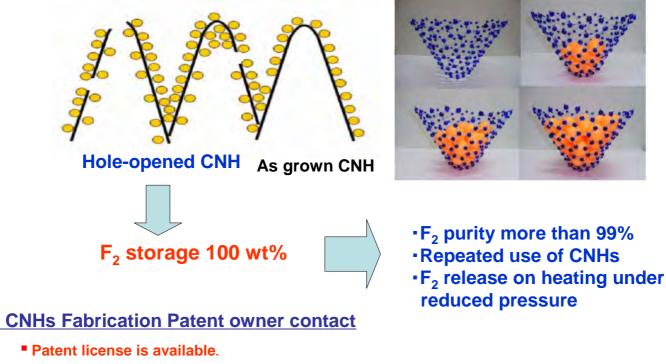
### Application

- Electrical conductors
- Drug delivery
- Li<sup>+</sup> capacitor battery
- Metal absorber
- Gas absorber ex. <u>Fluorine Gas</u>

Fluorine (F<sub>2</sub>) storage nano-cylinder

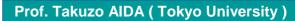
This research was sponsored by NEDO (New Energy & Industrial Technology Development Organization.

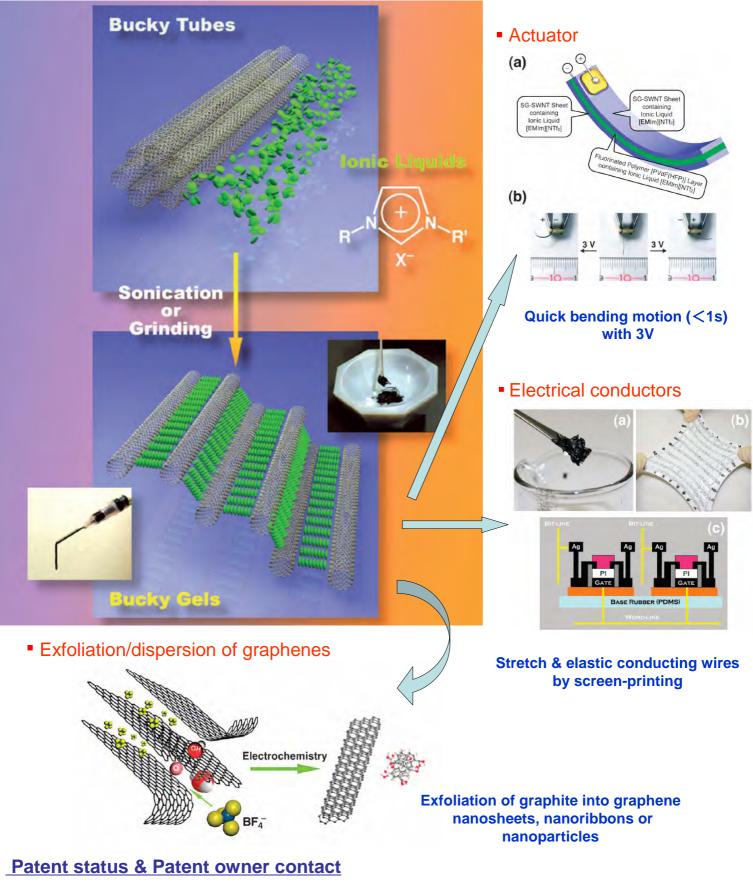
- Carbon nanohorns (CNHs) indicate the behavior of F<sub>2</sub> adsorption- desorption.
- Hole-opend CNHs is one of the best candidate as a nano-cylinder for F<sub>2</sub> storage which adsorbs 100 wt% F<sub>2</sub>/CNH and releases almost 100% of adsorbed F<sub>2</sub>.



Patent No. : JP4394383,US10/560808,EP4745618.1,CN200480016853.9; JP3479889,US10/483796,EP2746051.8,CN200202814122.9 Patent owner contact: Masaru OZAKI (JST) Tel:+81-3-5214-8486, e-mail: license@jst.go.jp

# Carbon Nanotubes Encounter Ionic Liquids to create New Soft Materials





Patent license is available.

Patent No. : US7531114, JP3676337, KR627184, CN200380101950.3, (EP1555242) Patent owner contact: Masaru OZAKI (JST) Tel:+81-3-5214-8486, e-mail: license@jst.go.jp

# Cycloparaphenylene (CPP)

### Prof. Kenichiro ITAMI (Nagoya University)

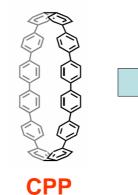
### **<u>1. CPP Molecular Structure</u>**

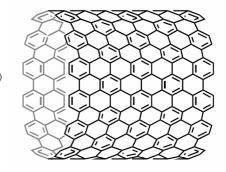
- Despite the structural simplicity and beautiful structure of CPP, no successful synthesis had been reported at the inception of our work.
- CPP has a potential precursors in the preparation of structurally uniform armchair or carbon nano-tube.



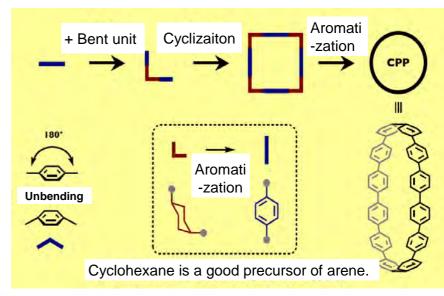
# 2. Synthesis of CPP

- Synthesis strategies are ;
  - 1) Using linear (arene) & bent (cyclohexane) units
  - 2) Using Pd-catalyzed Suzuki-Miyaura cross-coupling reactions to connect both linear and bent units
  - 3) Using acid for final transformation to CPP
- Our success in synthesis of CPP (n=9,12,14,15,16)





### **Carbon Nano Tube**



### 3. Patent Status & Patent contact

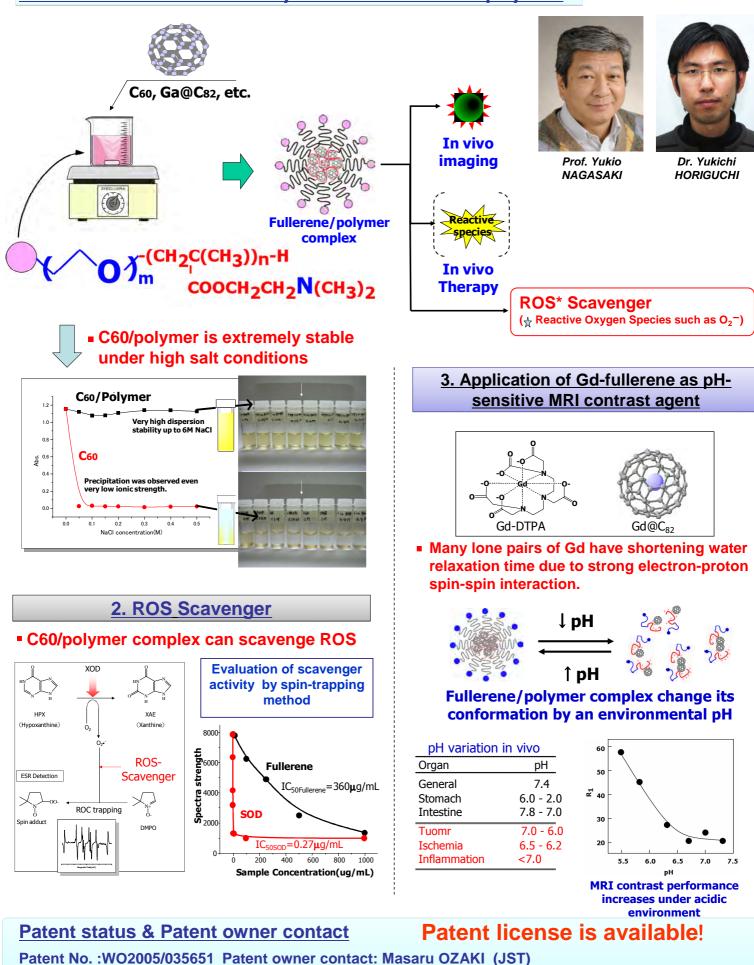
Patent license is available.

Patent No. : PCT/JP2011/052948, PCT/JP2011/055423 Patent contact: Masaru OZAKI (JST) Tel:+81-3-5214-8486, e-mail: license@jst.go.jp

# Water Soluble Fullerenes for Biomaterials

### 1. Solubilization of Fullerenes by water soluble block copolymers

University of Tsukuba

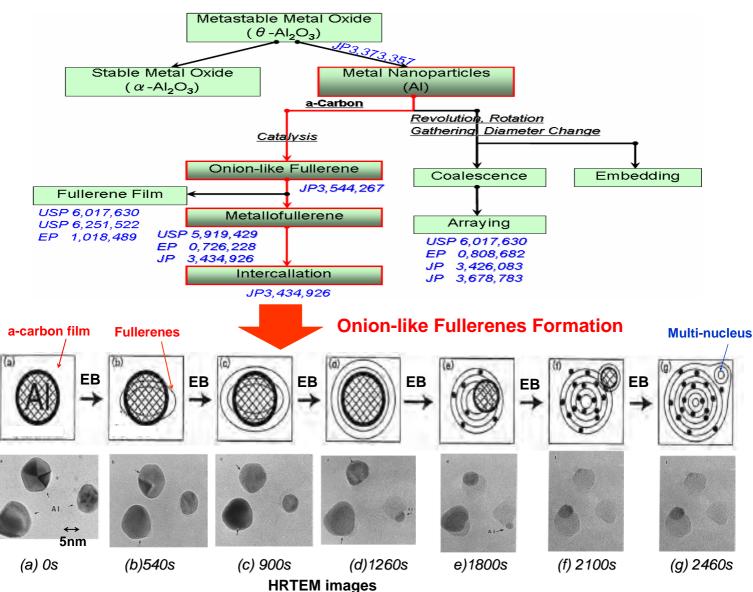


Tel:+81-3-5214-8486 e-mail: <u>license@jst.go.jp</u>

### Formation of Fullerene Nanostructures from Metastable Metal Oxides on a-C thin film by Electron Beam Irradiation

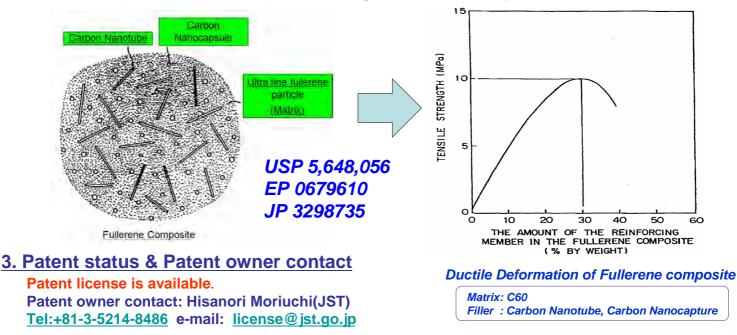


### 1. Formation of Various Fullerene Nanostructures



### 2. Fullerene Composite and its tensile strength reinforcement

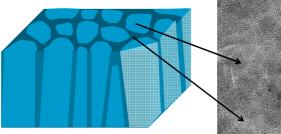
Fullerene Composite reinforces the tensile strength of C60 drastically



# Excellent Mechanical Properties of Hybridized Carbon Nano-composite Thin Films

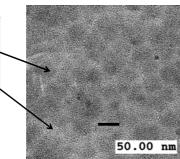
### **1. Fabrication of Hybridized Carbon Films**

Dr. Eiji IWAMURA (Arakawa Chemical Ind. Ltd.)



Column regions : d=1.8 g/cm3 Inter-column regions : d=1.6 g/cm3

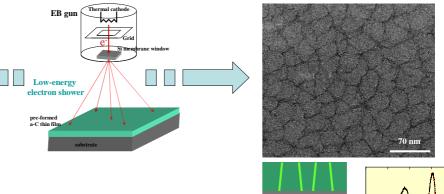
as deposited column



 Sputtering method is used under the conditions of both low temperature of substrate and high pressure of atmosphere gas for fabrication of network structures consisting of columns and inter-column regions in a-C films.

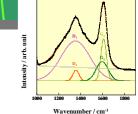
> Hybridized a-C film : Thickness: 500 nm Sputter deposited on Si wafer Substrate : Room temp. Ar+CH₄ gas pressure: 4Pa

### 2. Structural Modification by low-energy EB Irradiation



### Graphitization induced by EB irradiation

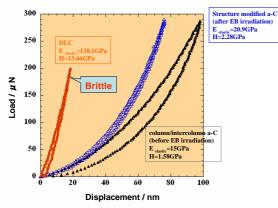
# After EB irradiation



### 3. Mechanical Properties of EB irradiated film

ber / cm-1

EB irradiated film shows not only superior wear resistance but high elasticity.



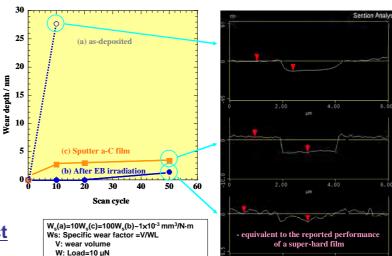
### Film hardness : Nanoidentation test

1400 1600

Wavenui

### Micro-wear resistance test

L: Total scan length~0.27cm



### 4. Patent status & Patent owner contact

 Patent license is available.
 Patent No. :WO2005/083144
 Patent owner contact: Masaru OZAKI (JST) Tel:+81-3-5214-8486
 e-mail: license@jst.go.jp

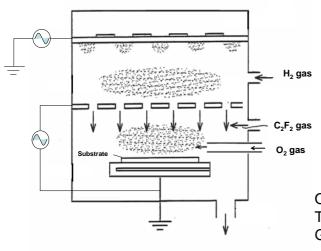
# Carbon Nanowall Substrate for Matrix-free Laser Desorption/Ionization Mass Spectrometry

Prof. Masaru HORI (Nagoya University) Dr. Hiroaki SATO (AIST)

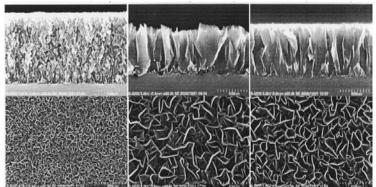
Carbon nanowall substrate, which is fabricated by RI-PECVD (Radical Injection Plasma-enhanced CVD), is very useful for matrix-free laser desorption ionization-mass spectrometry in which mass spectra can be easily observed without obstructive peaks and with good reproducibility.

### **1. Fabrication of Carbon Nanowall**

RI-PECVD Equipment



### Carbon Nanowall Substrate ; Low cost & Wide variation

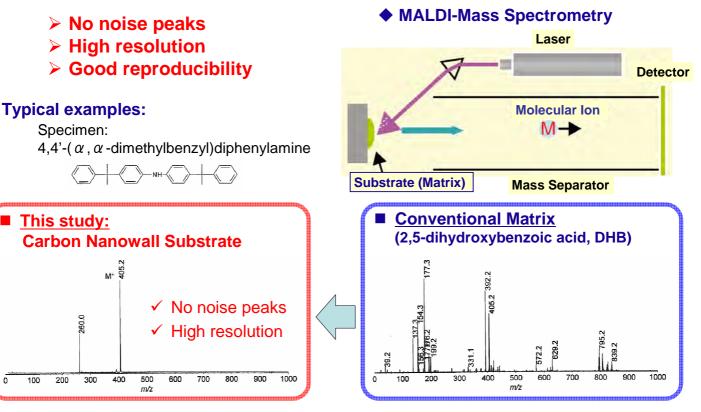


O<sub>2</sub>: 0 sccm (0%) Thickness: 1200 nm Growth rate: 60 nm/min

2 sccm (1.3%) 760 nm 19 nm/min

5 sccm (3.2%) 890 nm 22 nm/min

# 2. Mass Spectra using Cabon Nanowall



### 3. Patent status & Patent contact

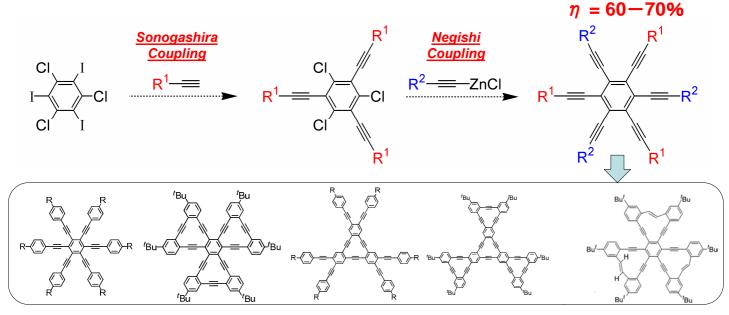
Patent license is available.
 Patent No. : JP2009-183797, PCT application
 Patent contact: Masaru OZAKI (JST)
 Tel:+81-3-5214-8486, e-mail: license@jst.go.jp

# Synthesis of Giant $\pi$ Conjugated Aromatic Compound

Prof. Yoshito TOBE (Osaka University)

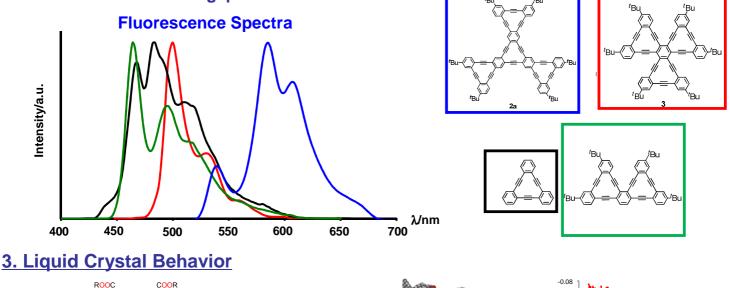
### **1. Synthesis of Substituted Hexaethynylbenzenes**

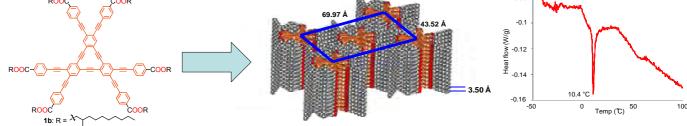
 Highly efficient synthesis method of differentially substituted hexaethynylbenzens from chloroiodobenzenes.



### 2. Emission Spectra

• Elongated  $\pi$ -conjugated compounds show red-shift emission spectra, which indicate small band gap.





### 4. Patent status & Patent owner contact

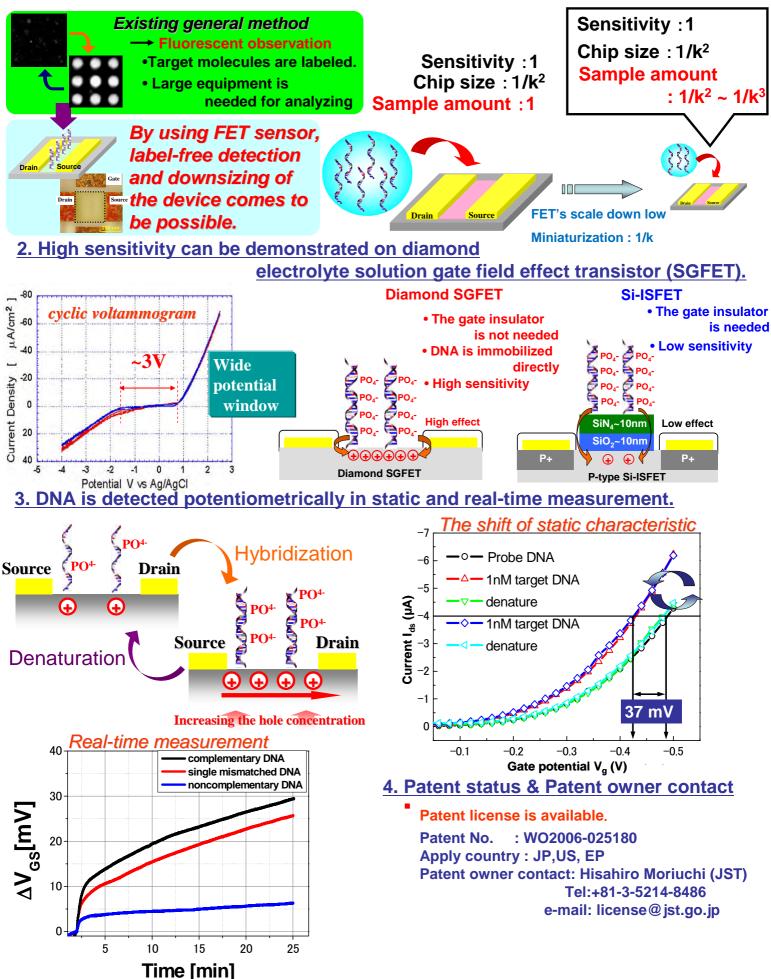
Patent license is available.

Patent No. : US6953871, JP4150168 Patent owner contact: Masaru OZAKI (JST) Tel:+81-3-5214-8486, e-mail: license@jst.go.jp

# **Diamond DNA Sensor**

Dr. Hiroshi KAWARADA (Waseda University)

### 1. Fast, easy, and lowcost label-free detection can be obtained by FET type sensor.

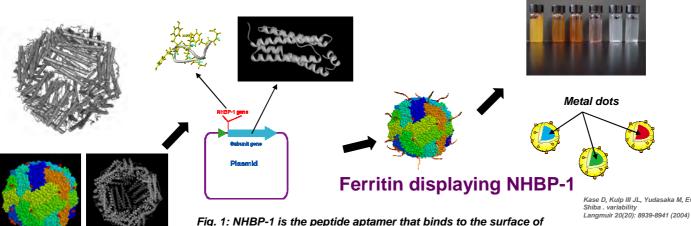


# Nanographite Structure/Metal Nanoparticle Composite

Kiyotaka SHIBA (JFCR), Kenichi SANO (RIKEN) and Kenji IWAHORI (NAIST)

The ferritin molecule displaying carbon nanohorn binding peptide-1 (NHBP-1) on its surface makes it possible to construct nanographite-metal nanoparticle composite by filling the interior of ferritin with metal dots.

### 1. Construction NHBP-1 displaying ferritin



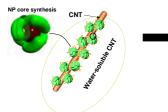
Ferritin

Fig. 1: NHBP-1 is the peptide aptamer that binds to the surface of nanographite. By fusing the peptide to the N-terminal of ferritin subunit, we can endow ferritin with graphite binding ability. Ferritin can be deposited with various metal nanodots in its inner space.

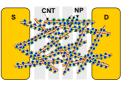
Kase D. Kulp III JL. Yudasaka M. Evans JS. liiima S.

Sano K. Aiima K. Iwahori K. Yudasaka M. Iiiima S. Yamashita I, Shiba K. Endowing a ferritin-like cage protein with high affinity and selectivity for certain inorganic materials Small 1 (8-9): 826-832 (2005)

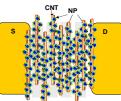
### 2. Making nanoelectronic devices using NHBP-1 displaying ferritin filled with metal dots.







CNT+Dps Random network



CNT+Dps parallel network

Fig. 2: Recently, Yamashita et al. at NAIST are using this technology to make novel type of electronic devices, in which they fused NHBP-1 to bacterial ferritin, Dps, and prepared the carbon nanotube (CNT)-semiconductor nanodots composites for novel type of electronic devices (personal communication).

### 3. Growing giant two-dimensional NHBP-1 displaying ferritin filled with metal dots.

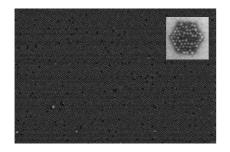


Fig. 3: NHBP-1 has a self-assembling ability that makes it possible to grow two-dimensional array of metalcontaining ferritin.

Matsui T, Matsukawa N, Iwahori K, Sano K, Shiba K, Yamashita I. Realizing a two-dimensional ordered array of ferritin molecules directly on a solid surface utilizing carbonaceous materials-affinity acatido Langmuir 23(4): 1615 -1618 (2007)

Ikezoe Y, Kumashiro Y, Tamada K, Matsui T, Yamashita I, Shiba K, Hara M. Giant growth of two-dimensional crystal of protein molecules from a three-phase contact line. Langmuir 24(22): 12836-12841 (2008)

### 4. Patent status & Patent owner contact

 Patent license is available. Patent No. : US-2010-0029910-A1 Patent owner contact: Yoshihiro Murai (JST) Tel:+81-3-5214-8486 e-mail:license@jst.go.jp

# Other Innovative Technologies



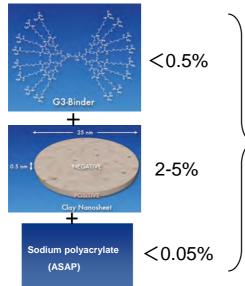
# **High-water-content Hydrogel**

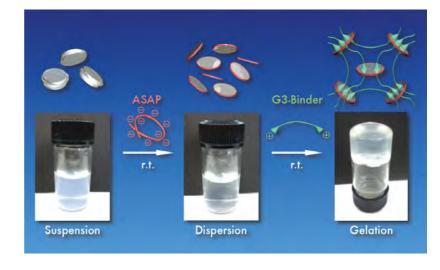
### **1. New Aqua Material**

- Mostly water (>95% Water ; <0.2% Organic )</p>
- Easily preparable
- Disposable (Environment friendly)
- Self-standing (Transportable)
- Self-healable
- Adhesive
- Transparent
- Non-flammable
- Capable of containing bioactivities

### 2. Preparation of New Agua Material

Aqua material can readily be prepared by mixing three components in water at RT.





### 3. Properties of New Agua Material

Moldable, Self-standing, & Transparent



### 4. Patent status & Patent owner contact

Patent license is available. Patent No. : PCT/JP2010/004267, JP2009-156670 **Apply country : Worldwide** Patent owner contact: Masaru OZAKI (JST)

### Comparison of Hydrogels

	Water Content	Content of Organic Components	Mechanical Strength	Required Skill (time)	Self-healable	Resistant to Organic Solvents
Double Network Hydrogel	90%	10%	17 MPa	Very High (2 days)	NO	YES
Nanocomposite Hydrogel	89%	8%	1 MPa	Very High (20 h)	NO	YES
Aqua Material (Our Hydrogel)	98% 95%	0,2%	0.1 MPa 0.5 MPa	Just Mixing (3 set)	3 sec (100%)	YES.
Oligoelectrolyte Hydrogel	97%	3%	0.01 MPa	Low (30 min)	10 sec (100%)	NO
Oligopeptide Hydrogel	99%	1%	0.00017 MPa	Low (overnight)	24 h (100%)	NO

### Application

- •Regenerated material for bone, cartilage etc.
- •Buffer material for sports shoes etc.
- Alternative rubber, plastic etc.
- Fire extinguishant etc
- . . . . . . .

Prof. Takuzo AIDA (Tokyo University)



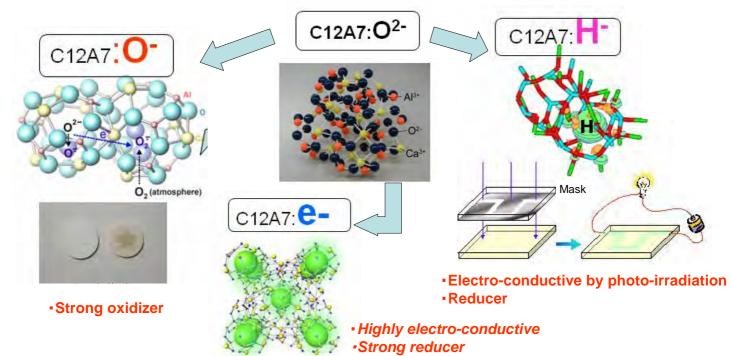
Tel:+81-3-5214-8486, e-mail: license@jst.go.jp

# Electro-conductive & Transparent Nano-porous Compound C12A7

Prof. Hideo HOSONO (Tokyo Institute of Technology)

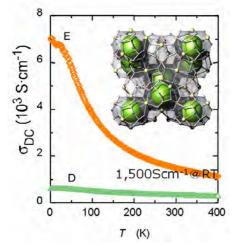
### 1. Novel Compound 12CaO·7Al<sub>2</sub>O<sub>3</sub> (i.e.C12A7)

- C12A7 is composed of materials of alumina cements, and has 6 cages with an inner free space of 0.4nm of which only one cage is filled by O<sup>2-</sup>. These 80% cages are free spaces.
- The oxide ions can be replaced by various anions such as O<sup>-</sup>, H<sup>-</sup>, OH<sup>-</sup>, e<sup>-</sup> etc and show very interesting functions.

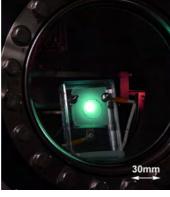


### 2. Electride C12A7: e<sup>-</sup>

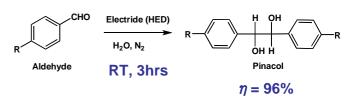
Conductivity of C12A7: e<sup>-</sup>



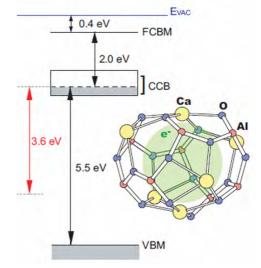
 Cathode ray emission from C12A7: e<sup>-</sup>



Reduction reaction using C12A7: e<sup>-</sup>



### 3. Small work function of C12A7: e-



### 4. Patent status & Patent owner contact

Patent license is available.

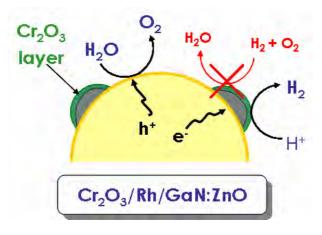
Patent No. :US6818192,7462334.7235225,7507289,7465433, EP1717217, JP4147324,4219821,4245608, TW283234 etc Patent owner contact: Masaru OZAKI (JST) Tel:+81-3-5214-8486 e-mail: license@jst.go.jp

# Photocatalyst Releasing Hydrogen from Water

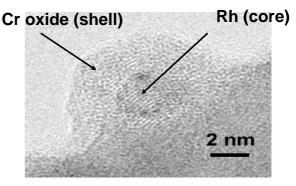
### Prof. Kazunari DOMEN (University of Tokyo)

### 1. Direct Splitting of Water by Visible Light

New catalyst is a solid solution of Ga-Zn-O (ex.Ga<sub>0.7</sub>Zn<sub>0.3</sub>N<sub>0.7</sub>O<sub>0.3</sub>) modified with nano-particles of Rh-Cr oxide

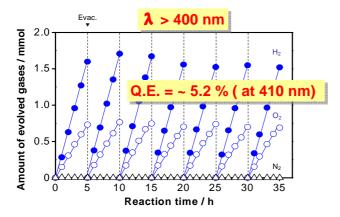


High resolution TEM image



Cr oxide/Rh/GaN:ZnO after Cr<sup>3+</sup> deposition

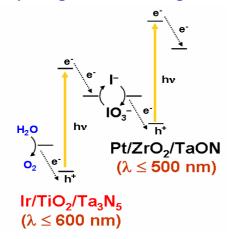
The quantum efficiency of water splitting by visible light is about 5% at 410nm





### 2. Improved Method for Higher Quantum Efficiency

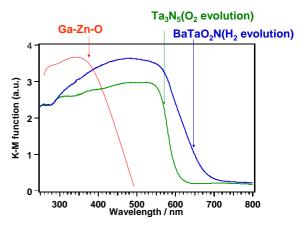
 Two step excitation system on water splitting under visible light



- 3. Patent status & Patent owner contact
  - Patent license is available.

Patent No. : USP6878666, 6864211, 6838413, 7015171, 7670712 Patent owner contact: Masaru OZAKI (JST) Tel:+81-3-5214-8486 e-mail: license@jst.go.jp

 Using photocatalysts to extend the absorption edge to longer wavelengths



# **Measurement of Water Isotopomers and its Applications**

### 1. Water Isotopomers (WI)

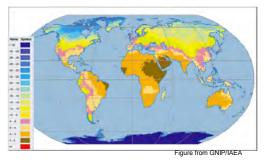
### Isotopomers of water molecule

<b>H</b> O	HOO O		2100
Isotopomer ratio	Rel. abundance	Conventional technique	Expressio n
HD <sup>16</sup> O/H <sub>2</sub> <sup>16</sup> O	0.03%	Reduction to $H_2$ $H_2$ equilibration with Pt catalyst Laser spectroscopy	δ D*1
H <sub>2</sub> <sup>18</sup> O/H <sub>2</sub> <sup>16</sup> O	0.20%	CO <sub>2</sub> equilibration Laser spectroscopy	δ <sup>18</sup> Ο
H <sub>2</sub> <sup>17</sup> O/H <sub>2</sub> <sup>16</sup> O	0.04%	Fluorination with $BrF_5$ (CoF <sub>3</sub> )	δ <sup>17</sup> O

\*1:  $\delta$  D (‰) = (D/H)\_{sample} / (D/H)\_{VSMOW} - 1 VSMOW: Vienna Standard Mean Ocean Water provided by IAEA and NIST/USA

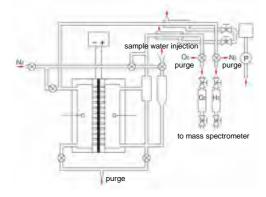
### Prof. Naohiro YOSHIDA (Tokyo Institute of Technology)

- Analysis of WI is applicable to;
- global environments
- traceability of foods
- medical cares
- criminal investigations



Global mapping of isotope ratio ( $\delta^{18}$ O) in precipitation

### 2. Rapid and Precise WI Analysis by Water Electrolysis Device (WED)

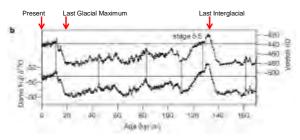


### Comparison with other techniques

	Equilibration	Fluorination (for O) Reduction (for H)	Laser Spectroscopy	WED
Advantage	Longest history Commercially available	Micro-liter sample Commercially available (reduction)	Micro-liter sample Fastest analysis	Fast analysis Micro-liter sample
Disadvantage	Slowest analysis Difficult for micro-liter	Chemical hazardous Difficult to control	Worst precision	
<sup>17</sup> O analysis	Possible but difficult	OK (by fluorination)	Impossible	ОК

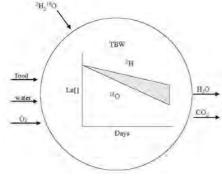
### 3. Applications of WI Analysis-Environment, Food and Human Diagnosis

### Historical change of global temperature reconstructed from Antarctic Ice Core.

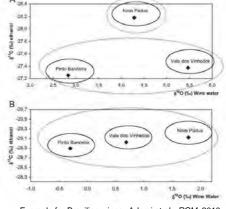


Watanabe, Yoshida, et al. (Nature, 2003)

### Metabolic energy measured by doubly labeled water (DLW) method



Geographic origin (cultivation regions) identified using  $\delta$  180 of wine water.



Example for Brazilian wines Adami et al., RCM, 2010

### 4. Patent status & Patent owner contact

Patent license is available.

Patent No. : WO00/49640, WO00/58712 Apply country : JP,US, EU Patent owner : JST, Tokyo Institute of Technology

Contact: O.KANZAKI (JST) Tel:+81-3-5214-8486 e-mail: license@jst.go.jp

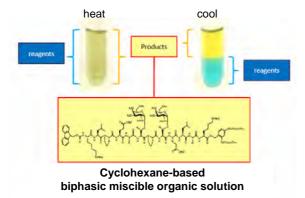
Schoeller, International J. Obesity, 2008

# A Novel Technology for Solution Phase Peptide Synthesis

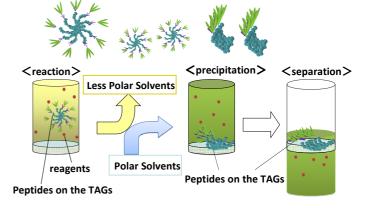
Dr. Kazuhiro CHIBA (Tokyo University of Agriculture and Technology)

### 1. Introduction

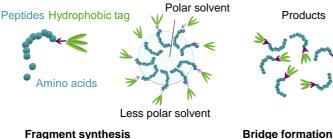
**Basic Technology** Chemical Synthesis in biphasic miscible organic solution



**Example of Application** Product Separation in biphasic immiscible solvents



### 2. Application for peptide synthesis





HBTU HOBt CH<sub>2</sub>Cl<sub>2</sub> N-Arg(Mts)-Pro-O-TAGc DBU Piperidir CH<sub>2</sub>Cl<sub>2</sub> H-Asp-Phe-Leu-Pro-His-Tyr-Lys-Asn-Thr-Ser-Leu-Gly-His-Arg-Pro-OH

Synthesis of a TNF-a Antagonist

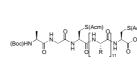
### Synthesis of Somatostatin

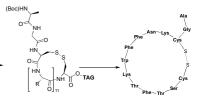


Up to equimolar reactions

Varied modifications

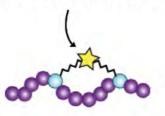






### 3. Peptune<sup>TM</sup> (commercially available product) approach

Introducing a new bridge chemistry with linker function to introduce steric constraint



Functional moiety can be appended on bridgehead position in addition N, C terminal position

Peptune<sup>™</sup> provides new peptide scaffolds with artificial bridge which is;

1. introducing other functional moiety into peptide's backbone as well as controlling structural constraint of peptides

2. as a similar approach to medicinal chemistry

3. with a unique liquid phase synthesis method

4. applicable to peptide therapeutics, delivery motives, and diagnostics

### 4. Patent status & Patent owner contact

Patent license is available. : 3538672(JP) and others Patent No. Applied in : JP,US,EP,CN Patent owner contact : Osamu KANZAKI Tel: +81-3-5214-8486 e-mail: license@jst.go.jp Peptune patent filed in worldwide by JITSUBO Co.Ltd., a Japanese licensee of JST for the basic patent and also available for licensing.

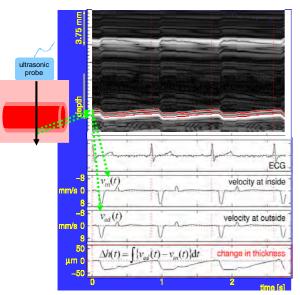
### **Ultrasonic Elasticity Imaging of Arterial Wall** for Tissue Characterization

### [Summarv]

Diagnosis of vulnerability of atheroma is important for prevention of cardiovascular and cerebrovascular events. We have developed a method for measurement of the regional elasticity of the arterial wall with transcutaneous ultrasound. This method has potential for noninvasive tissue characterization of artery wall.

### [Phased Tracking Method]

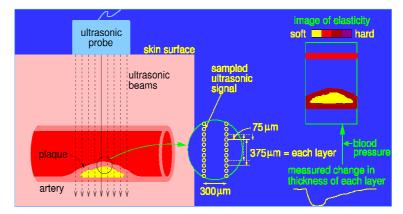
for measuring small change in thickness (strain) of artery wall caused by heartbeat



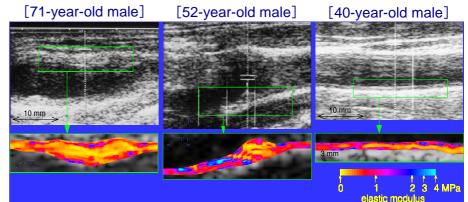
### [Elasticity Imaging]

Prof. Hiroshi KANAI (Tohoku University)

by measuring spatial distribution of changes in thickness (strain) and systolic/diastolic blood pressure measured with cuff at brachial artery



### [Transcutaneously Measured Carotid Elasticity Images]



**(Transcutaneous Tissue Characterization)** 

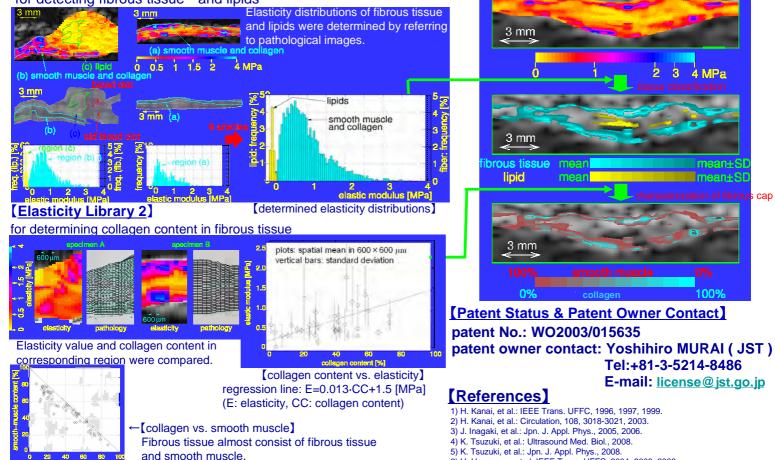
4 MPa

an±SI

100%

s cap

[Elasticity Library 1] %fibrous tissue=mixture of collagen and smooth muscle for detecting fibrous tissue\* and lipids



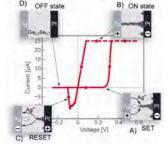
5) K. Tsuzuki, et al.: Jpn. J. Appl. Phys., 2008.
6) H. Hasegawa, et al: IEEE Trans. UFFC, 2004, 2006, 2008.

# **Atomic Switch Arrays for Memory and Logic Circuits**

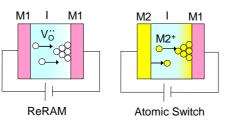
### Dr. Tsuyoshi HASEGAWA (National Institute for Material Science)

### 1. Nanoionic Devices

Nonvoaltile switches for memory and logic operations in the beyond 16nm generation.

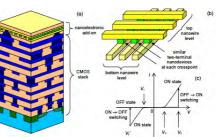


Filament formation and annihilation



ReRAM : Anion-based resistive switch Atomic Switch: Cation-based resistive switch

Specifications



Hybrid CMOS/Nanoelectronic circuit

### 2. Cation-based resistive switch: Atomic switches

itch ON

Two types of atomic switches.

### Gap-type atomic switch

Gapless-type atomic switch



### Scalability: 10 nm Switching time: 1 ns.

**Retention time: 10 years** Cyclic endurance: 10<sup>5</sup> times

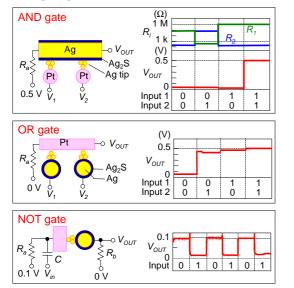
### **Materials**

Active Electrode: Cu, Ag

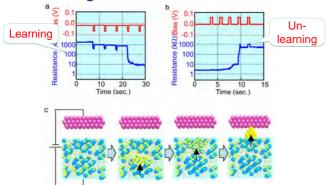
### 3. Application of atomic switches

### Logic gates

Cu Cu<sub>2</sub>S P

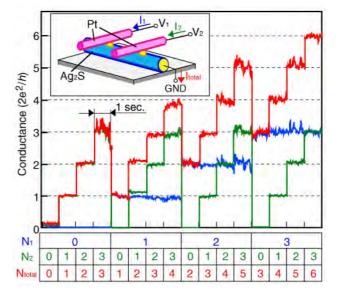


### Learning abilities



Multi-state memories, adder circuit, etc.

Ionic conductor: Ag<sub>2</sub>S, Cu<sub>2</sub>S, Ta<sub>2</sub>O<sub>5</sub>, HfO<sub>2</sub>, SiO<sub>2</sub>,



### 4. Patent status & Patent owner contact

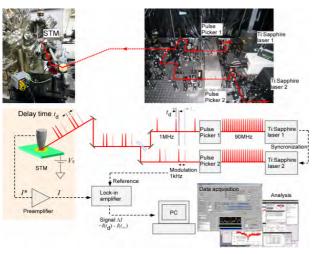
Patent license is available.

: WO2002-037572 Patent No. Apply country : JP,US,TW,EP,KR Patent owner contact: Hisahiro Moriuchi (JST) Tel:+81-3-5214-8486 e-mail: license@jst.go.jp

# New Pump-probe Technique providing a Wide Range Time-scale and Nanoscale Measurement

### 1. New pump-probe technique

### Delay Time Modulation Femtosecond Time-resolved Scanning Probe Microscope



(1)Conventional optical intensity modulation causes the tunnelling current change by the thermal effect.

(2)Delay time modulation using pulse pickers gives:

①wide time rage measurement (femtosecond ~microsecond)
 ②overcome of the thermal effect

③temporal resolution deternined by pulse width and spatial resolution determined by STM

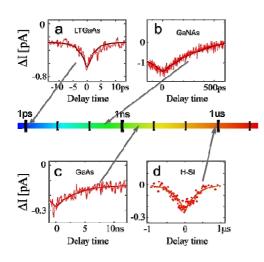
### 3. Examples by nanoscale pump-probe

Real space imaging of transient carrier dynamics in the nanostructures with a wide variety of lifetimes

### 3-1. Carrier lifetimes measured by STM

 $\boldsymbol{\cdot} \textsc{Time-dependent}$  STM signals can be obtained for various materials

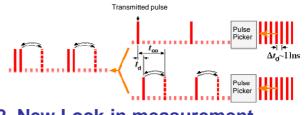
• Decay times of photoexcited carriers are consistent with the lifetimes measured by conventional optical pump-probe method.



### Prof. Hidemi SHIGEKAWA (University of Tsukuba)

### 2. new key method 2-1. new delay-time modulation

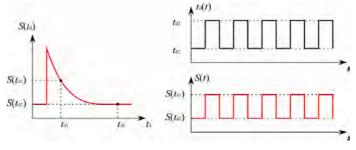
Delay time is controlled in a digital form using pulse pickers.



### 2-2. New Lock-in measurement

Delay time  $t_d$  is modulated between  $t_{d1}$  (measurement point) and a large value of  $t_{d2}$ . The signal  $S(t_d)$  is measured by lock-in detection technique.

The output of the lock-in amplifier directly provides  $S(t_{d1})$ .



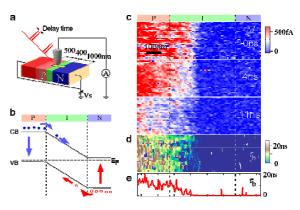
### 3-2. Imaging nanoscale carrier dynamics

Observation of diffusion and drift on carrier recombination processes in an inner potential of GaAs PIN structure: Decay of photocarrier density is apparently accelerated in the I-region.

a: measuring method. b: band structure.

c: a series of time-dependent carrier density images.d: mapping of decay time obtained from the full series of the time-dependent STM images.

e: decay time  $\tau_{d}$  (cross section along the line in d.)



### 6. Patent status & Patent owner contact

### Petent license is available.

Patent No. :①WO 2008/066090,②WO 2003/046519 Apply country :①JP,US,EP,CA,CN,KR②JP,US,EP Patent owner contact: Hisahiro Moriuchi (JST) Tel:+81-3-5214-8486 e-mail: license@jst.go.jp

### Electronic State Calculation Method, Computer Program, by Fluctuation-Referenced Multi-Reference DFT

### 1. What is MR-DFT?

Our MR-DFT realizes

- Inclusion of quantum fluctuation,
- Systematic improvement of LDA, etc.

	Single-referenced Kohn- Sham DFT-LDA	Multi-referenced extended KS DFT
Reference	W. Kohn and L.J. Sham, Phys. Rev. <b>140</b> (1965) A1133.	K. Kusakabe, JPSJ <b>70</b> (2001) 2038; <i>ibid</i> <b>78</b> (2009) 114716.
Formal self-consistency in calculation scheme	0	0
Ab-initio determination of model functionals	Extrapolation	0
Variational principle for model functionals	×	0

### 3. New technique developed!

Production of a model sequence in the model space (a Banach space).

A schematic example

Exact solution of electron system with Coulombic correlation

Quantum fluc. in full bands •Multi-band correlation

### Convergence area

Quantum fluc. around E<sub>F</sub> •CDW, SDW •Super. or MI tr. Quantum fluc. in many bands •Multi-band ex-Hubbard

### A quantum phase transition

DFT LDA, GGACharge dens.Spin densityBand structure

Quantum fluc. In an isolated band •Single band Hubbard model

Convergence w.r.t. charge distance  $\Rightarrow$  a converged model in the model space.

Theorems: J. Phys. Math. Theor. **44** (2011) 135305. K. K. & I. Maruyama: Japan patent submitted : JP 2010-183375.

### 5. Patent status & Patent owner contact

### Patent license is available.

Patent No. : WO2010-023943 Apply country : JP, US(allowed) Patent owner contact: Hisahiro Moriuchi (JST) Tel:+81-3-5214-8486 e-mail: h2moric@jst.go.jp

# 2. How MR-DFT is given?

• Based on an energy functional, =  $\begin{bmatrix} 1 & \cdots & (\infty)^{\frac{1}{2}} \\ \sum -(0)^{\frac{1}{2}} \\ \sum -(0)$ 

Prof. Dr. Koichi KUSAKABE (Osaka University)

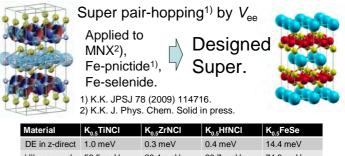
- $F_{X_i}[n] = \min_{\Psi \to n(\mathbf{r})} \langle \Psi | \hat{T} + \sum_{n} \Xi_n^{(i)} \left( \hat{Y}_n^{(i)} \langle \hat{Y}_n^{(i)} \rangle, \hat{Z}_n^{(i)} \langle \hat{Z}_n^{(i)} \rangle \right) \Psi \rangle.$ 
  - JPSJ 70 (2001) 2038.
- Variational principle is given.
  - JPSJ 78 (2009) 114716.

and calc. with corr. relevant bands.	Convergence check	
	Self-consistent solution	

### 4. Applications

in

### Layered superconductors with high $T_{\rm c}$



DE INE GROOT		0.0	0	
J'  upper only	56.5 meV	26.4 meV	20.7 meV	74.8 meV
J'  total	65.6 meV	34.7 meV	26.4 meV	164 meV

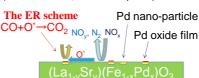
$$F_{n_{1},\mathbf{k}_{1},n_{2},\mathbf{k}_{2}} = \left\langle \phi_{n_{1},\mathbf{k}_{1}}\phi_{n_{2},\mathbf{k}_{2}} \left| \hat{V}_{ee} \right| \varphi_{n_{c},(\mathbf{k}_{c},l=0)} \varphi_{n_{c},(-\mathbf{k}_{c},l=0)} \right\rangle$$

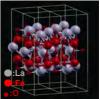
$$J' = -\sum_{n_1 \neq n_c, \mathbf{k}_1} \frac{\left|F_{n_1, \mathbf{k}_1, n_1, -\mathbf{k}_1}\right|^2}{\left|\mathcal{E}_{n_1, \mathbf{k}_1, n_1, -\mathbf{k}_1} - \mathcal{E}_{n_c, (\mathbf{k}_c, k_z)}\right|^2}$$

Convergence certified by our patent.

# New 3-way catalytic reaction

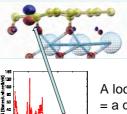
NO<sub>x</sub> reduction on LaO/LaFeO<sub>3</sub>. (H. Kizaki & K.K., Surf. Sci. in press.)





K.K. & H.Kizaki: Japan patent submitted : JP 2009-204665. A solution for the element science & technology.

# Design of graphene devices



# The array of Quantum dots in 200Tbit/cm<sup>2</sup> is expected!

A localized orbital = a quantum dot



Convergence certified by our patent.

: Periodic Anderson model by our patent.

# **Lignin-based Solar Cell**

### 1. Utilization of Forest Resources

### Prof. Masamitsu FUNAOKA (Mie University)

LPs

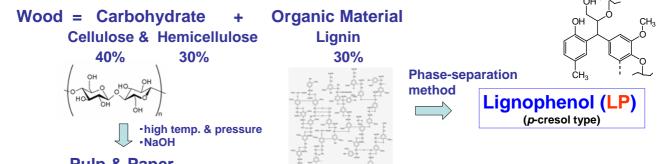
 $(\sim)$ 

interaction

like p-complex

e

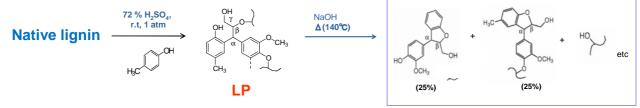
Lignin has never been utilized sufficiently as industrial material.



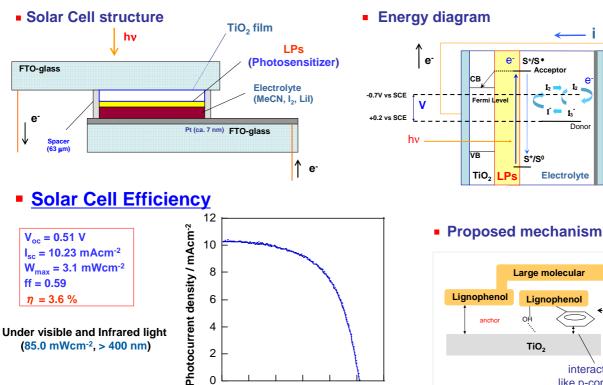
**Pulp & Paper** 

### 2. Phase-separation Method

Easy Separation of Carbohydrates and Lignin Derivatives



### 3. Lignin-based Solar Cell Structure



0.2 0.3 0.4 0.5 0.6

Photovoltage / V

# 4. Patent status & Patent owner contact

2

0

0 0.1

Patent license is available.

: WO2004/070868, JP3934068 Patent No. Apply country : JP,US,EP,KR,CN Tel:+81-3-5214-8486 Patent owner contact: Masaru OZAKI (JST)

e-mail: license@jst.go.jp



# Japan Science and Technology Agency Center for Intellectual Property Strategies 5-3, Yonbancho, Chiyoda-ku, Tokyo, 102-8666 JAPAN Phone: +81-3-5214-8486 Fax: +81-3-5214-8417 E-mail: license@jst.go.jp URL: http://www.jst.go.jp/tt/EN/univip/cips/licensing.html