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10 - 28 August 2009

A Novel Charged Medium Consisting of Gas-Liquid Interfacial Plasmas

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A Novel Charged Medium Consisting of Gas-Liquid Interfacial Plasmas

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Tohoku University, Sendai/Japan

1. Introduction

– **from gas-solid, via liquid-solid toward gas-liquid interfacial plasmas** –

2. – Liquid-Solid Interface –

Renewal of Electrolyte-Plasma Concept

3. – Liquid-Gas Interface –

Innovating Liquid-Gas Interfacial Plasmas

– Novel Charged Medium –

looking for a unique plasma-physics field

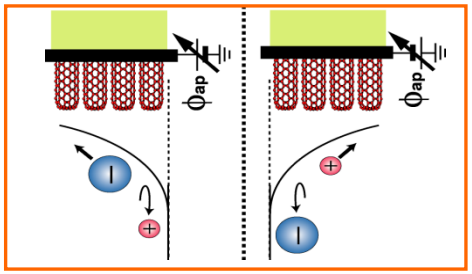
4. Application of Liquid-Gas Interfacial Plasmas

5. Summary

1. Introduction

– from gas-solid, via liquid-solid toward gas-liquid interfacial plasmas –

Backgrounds and Motivation



Gas-Solid Interfacial Region

Gas Phase Discharge Plasmas

Gas-Liquid Interfacial Region

Ionic Liquids

Nanocarbons

Liquid Phase Discharge Plasmas

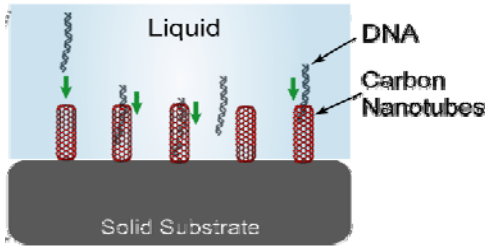
Cation (DNA base etc.)

DNA

Particle

Anion

Solid-Liquid Interfacial Region



Colloids

DNA

Protein

Biomolecules

Carbon nanotubes

Fullerenes

Nanocarbons

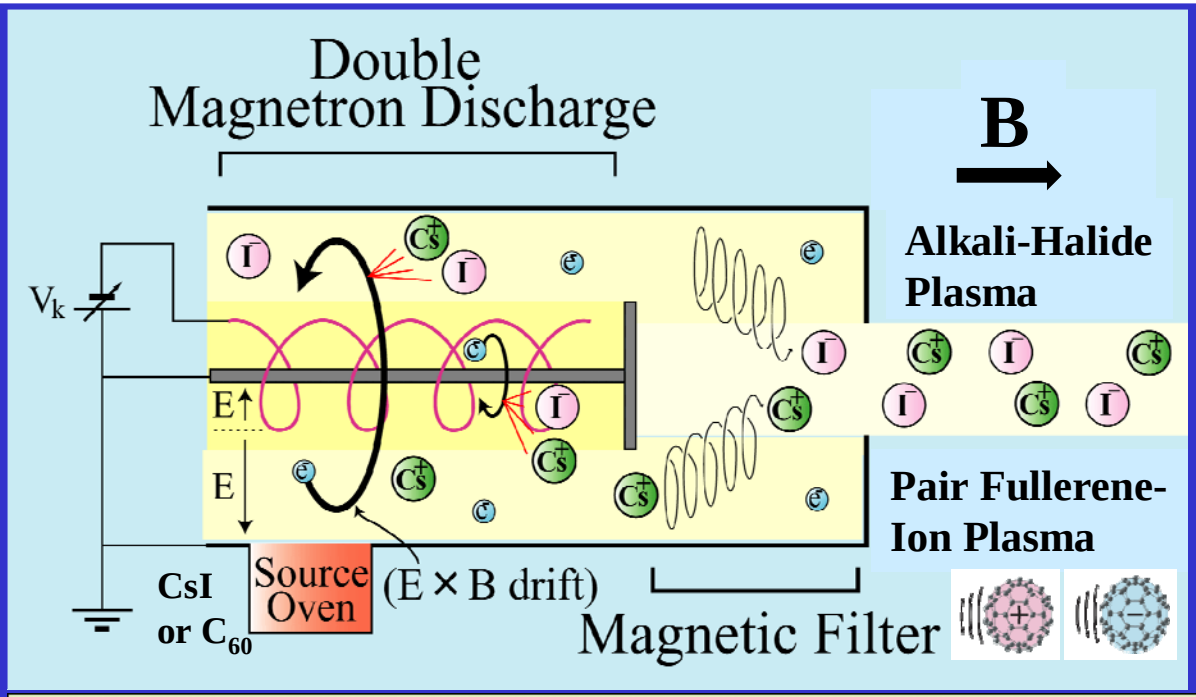
Combination of Materials Stable in Liquids and Nanocarbons [1]

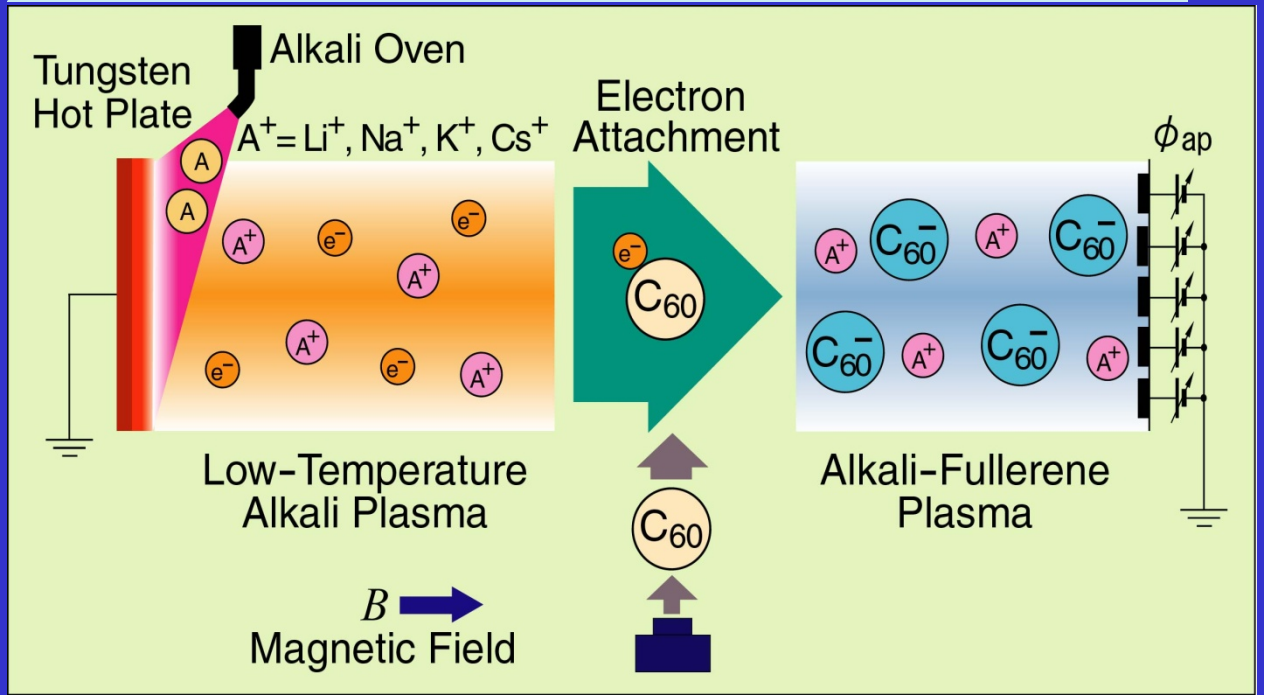
Creation of novel functional nano-bio composite materials

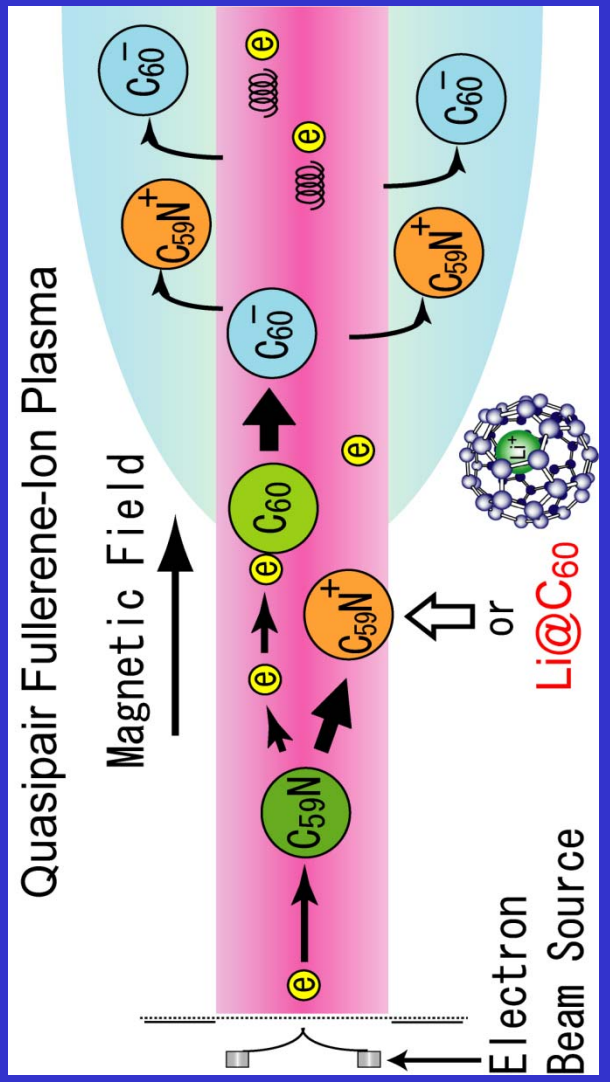
Nano-Compsite Materials
(Biomolecules/Metal Particles/Nanocarbons)

[1] Contrib. Plasma Phys. **47** (2007) 57; Nano and Molecular Electronics Handbook, CRC Press, London (2007), p. 4-1.

Ion Plasmas (Alkali–Halogen, Alkali–Fullerene, Pair Fullerene-Ion, Quasipair Fullerene-Ion)







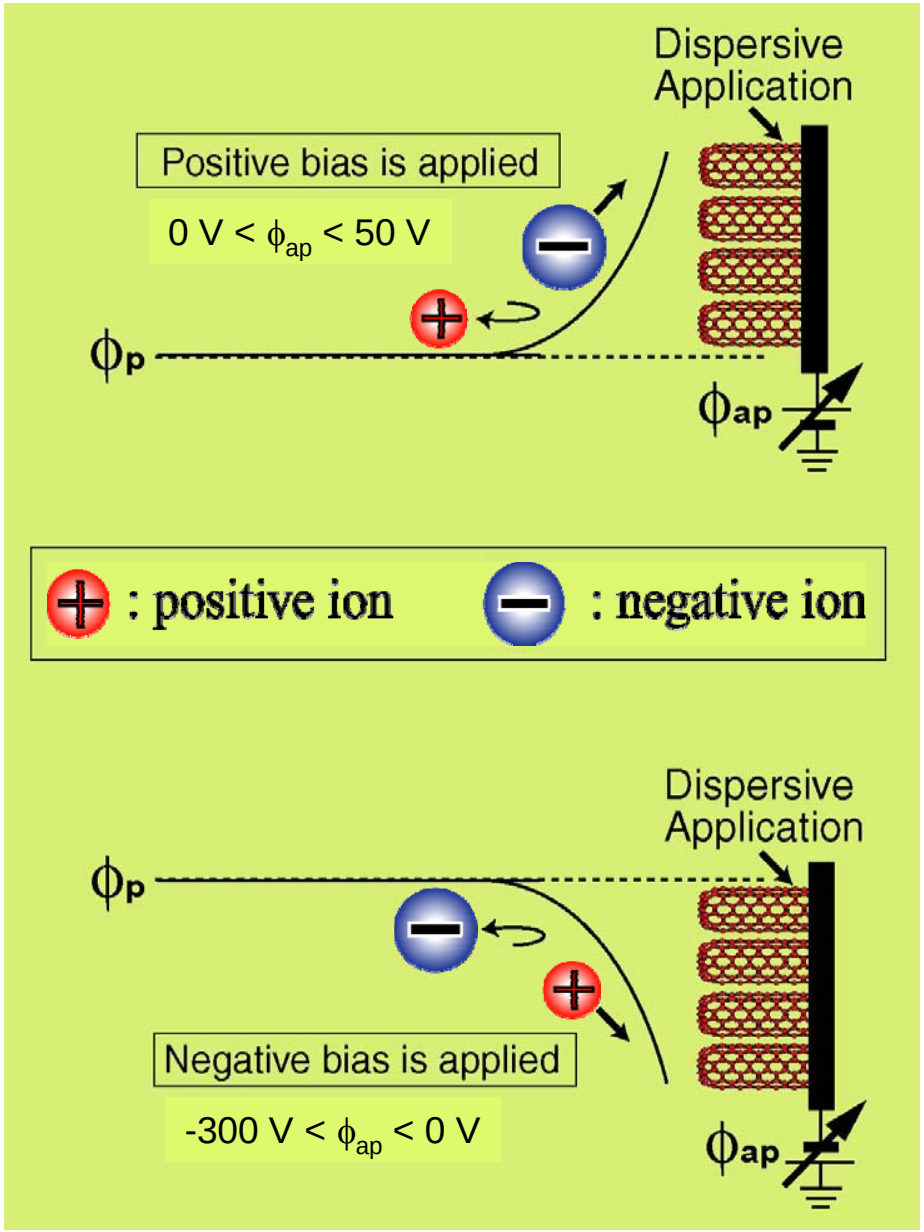
Appl. Phys. Lett. **88** (2006) 191501

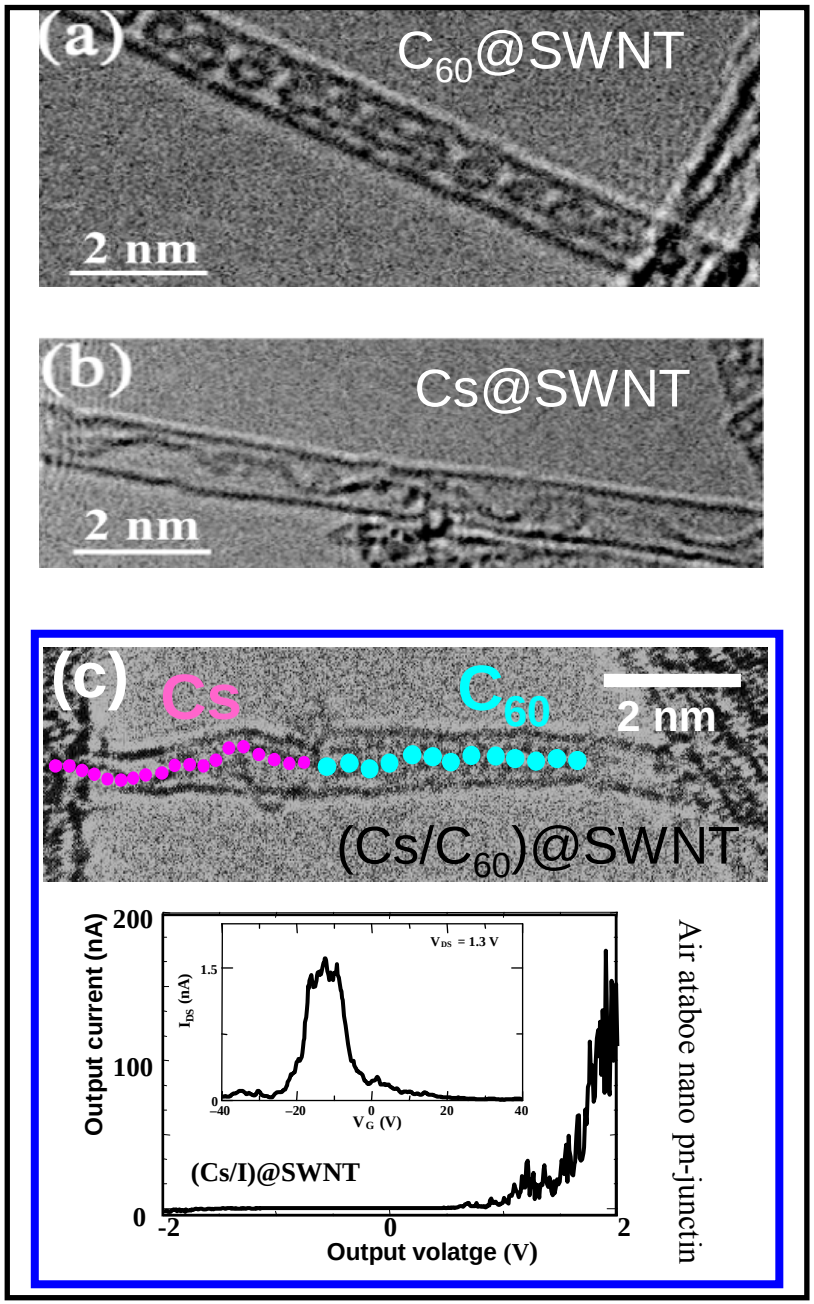
Phys. Rev. Lett. **91** (2003) 205005;
95 (2005) 175003.

J. Vac. Sci. Technol. A **14** (1996) 615

Nanospace Control of Carbon Nanotubes Using Gaseous Plasmas

Substrate bias method: Plasma-ion irradiation



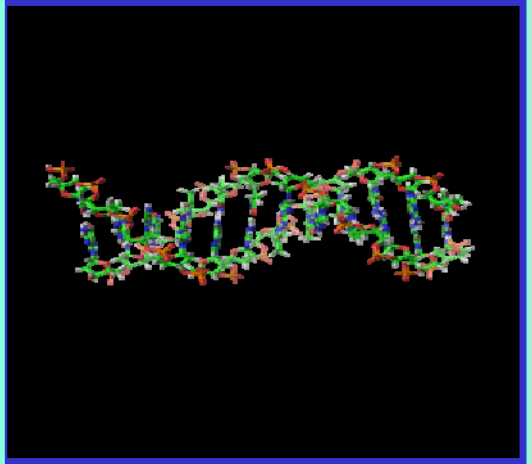


Appl. Phys. Lett. **79** (2001) 25; Phys. Rev. **B 68** (2003) 075410; Phys. Rev. Lett. **99** (2007) 256407; J. Am. Chem. Soc. **130** (2008) 2714

2. - Liquid-Solid Interface -

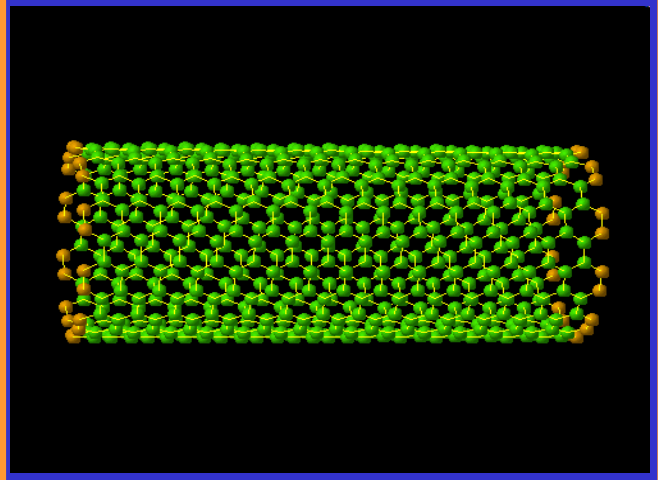
Renewal of Electrolyte-Plasma Concept

⇒ fusion between DNA and carbon nanotubes

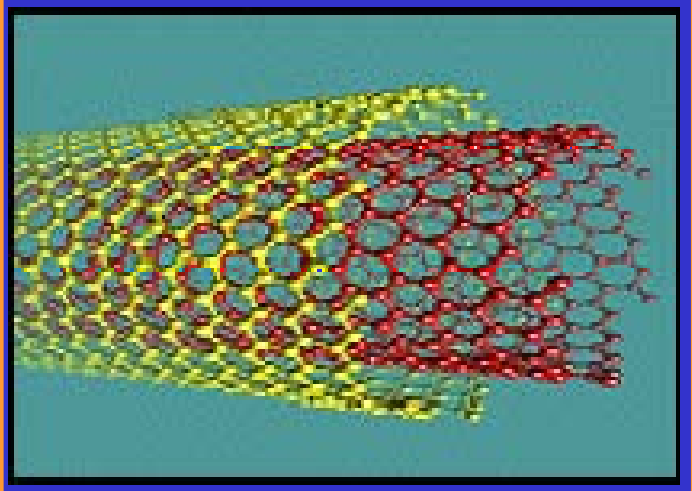


DNA

Diameter: ~ nm
Length: < nm ~ μm ~ mm



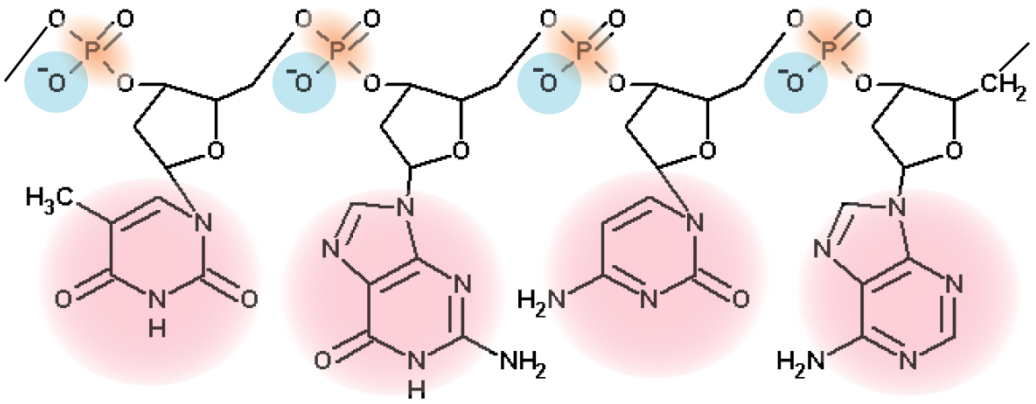
SWNT: single-walled nanotube



DWNT: double-walled nanotube

Structure of DNA Molecule

Single-stranded DNA



Thymine **Guanine** **Cytosine** **Adenine**

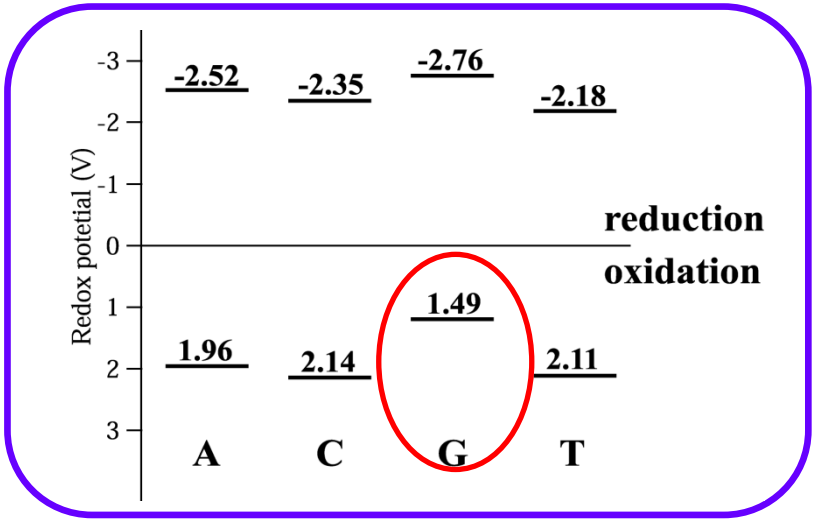
Phosphoric acid group

Negative charge

Bases

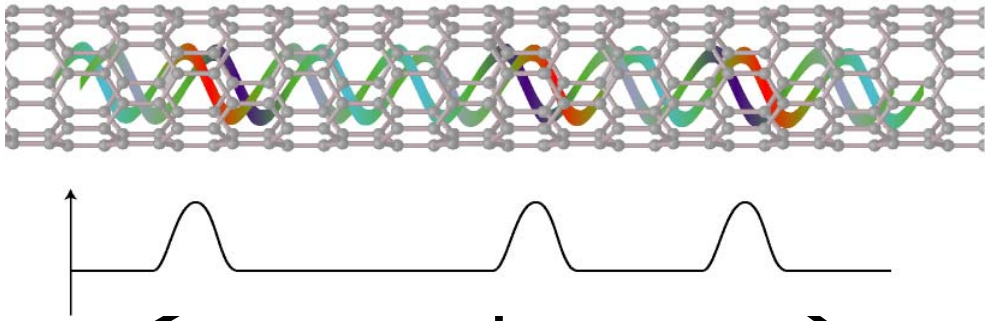
Number of phosphoric acid group
= electric charges
= bases
→ Chain length (10 bases = 3.4 nm)

Electronic Properties of Bases



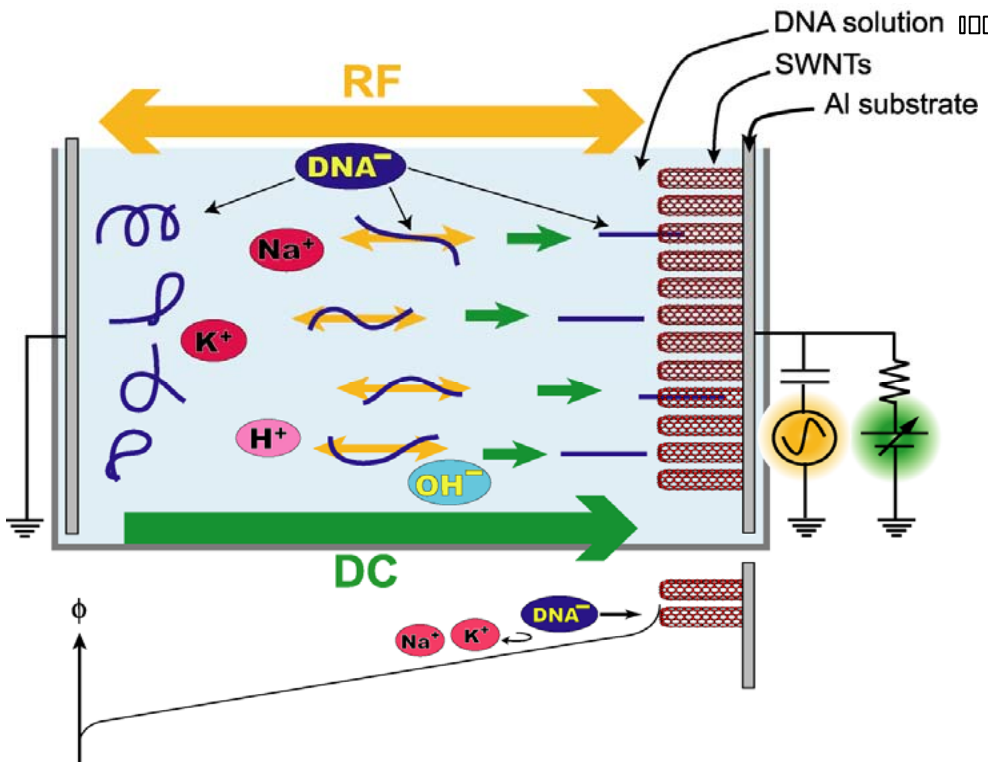
K. -H. Yoo *et al*. Phys. Rev. Lett. 87 (2001) 198102

DNA encapsulated carbon nanotubes

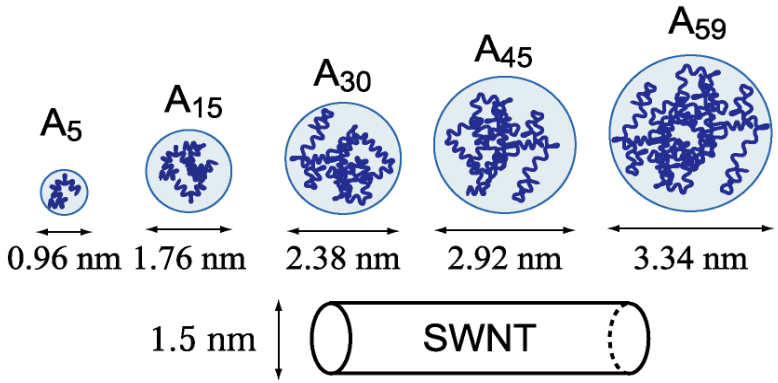


Gene delivery **Electronic devices** **Bio sensor**

Solution Plasmas for Bio/Nano Applications



DNA Electrolyte Plasmas



- DC for irradiation of DNA
- RF for stretch of DNA

DNA negative ion irradiation

DNA@SWNTs

RF Frequency	1 MHz
RF Voltage (V_{RF})	0-250 V
DC Voltage (V_{DC})	0-20 V
Electrodes	Aluminum
Electrode Gap	1000 μm
SWNTs	Heat treatment (470 °C / 30 min.)
DNA	Single-stranded DNA (Adenine & Guanine; $A_{5\text{-}59}$, AG_{30})

Ion-neutral collision

→ Necessity of strong electric fields

→ Micro electrolyte plasmas

Contrib. Plasma. Phys. 47 (2007) 57

Electrolyte Plasmas

Gas | **Electrolyte** [1]

	Gas		Liquid
Species	Electrons, ions, neutral particles		Ions, neutral particles * 1
Charge	Neutral		Neutral
	Q-Machine	DC discharge	Electrolyte
T	0.25 eV	3.0 eV	0.025 eV (300K) * 2
n	10^9 cm^{-3}	10^{10} cm^{-3}	~ 10^{15} cm^{-3} * 3
λ_D	~ 0.1 mm	~ 0.1 mm	~ 10 nm * 4
Γ	<<1		2~4
$\omega\tau$	>1		<1
λ_{mfp}	~ 1-10 m	~ 10-100 cm	<1 nm

* 1 : pH=7.0 ([H^+]=[OH^-]=10^{-7} mol/l),
H_2O: 3×10^{22}
H^+: 3×10^{13}
OH^-: 3×10^{13}
* 2 : Room temperature
* 3 : DNA solution (c = 35 μg/ml)
* 4 : λ_D = 1.2μm (w/o DNA)

$$\Gamma = \frac{q^2}{4\pi\varepsilon_0 d\, kT}$$

$$\lambda_D = \left(\frac{k_B T}{4\pi e^2 n}\right)^{1/2}$$

$$\lambda_D = \left(\frac{k_B T}{4\pi e^2 I}\right)^{1/2} \qquad I = \frac{1}{2}\sum_j c_j z_j^2$$

c: concentration , ***z***: charge

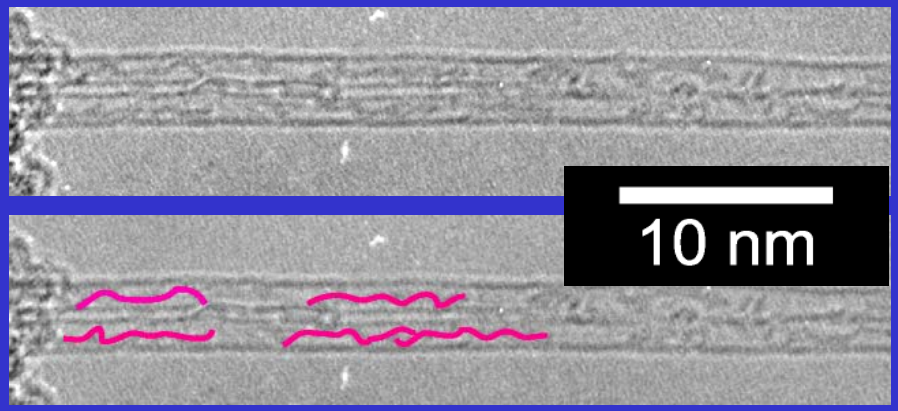
Electrolyte solution = Electrolyte plasmas

[1] P. Debye and E. Huckel, Physkalische Zeitschrift **24** (1923) 185

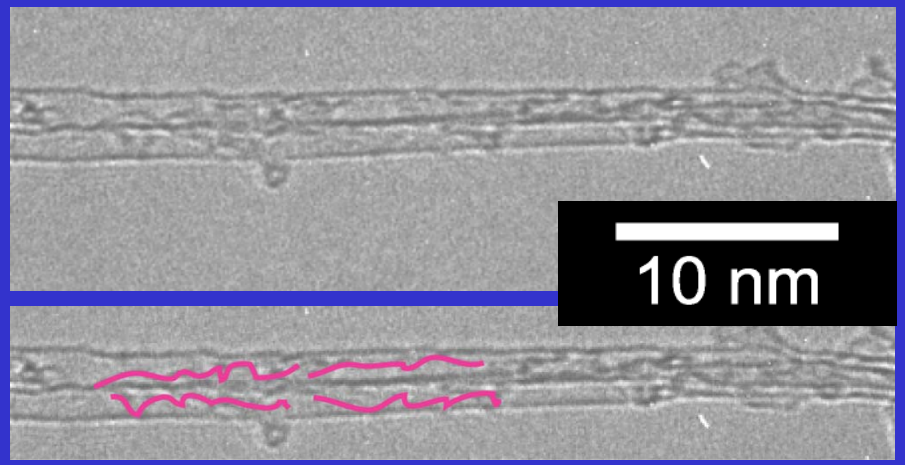
Transmission Electron Microscopy (TEM) Observation/Analysis

SWNTs

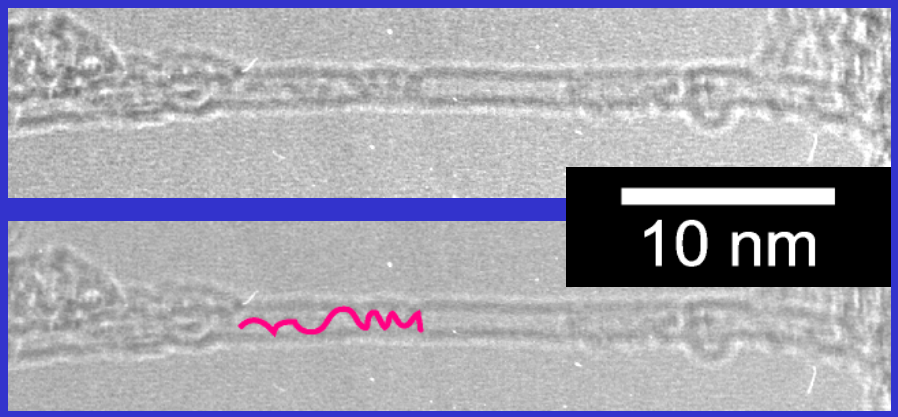
Adenine (A_{15}~ 5 nm)



Adenine (A_{45} (~15 nm)



Adenine (A_{30}~ 10 nm)



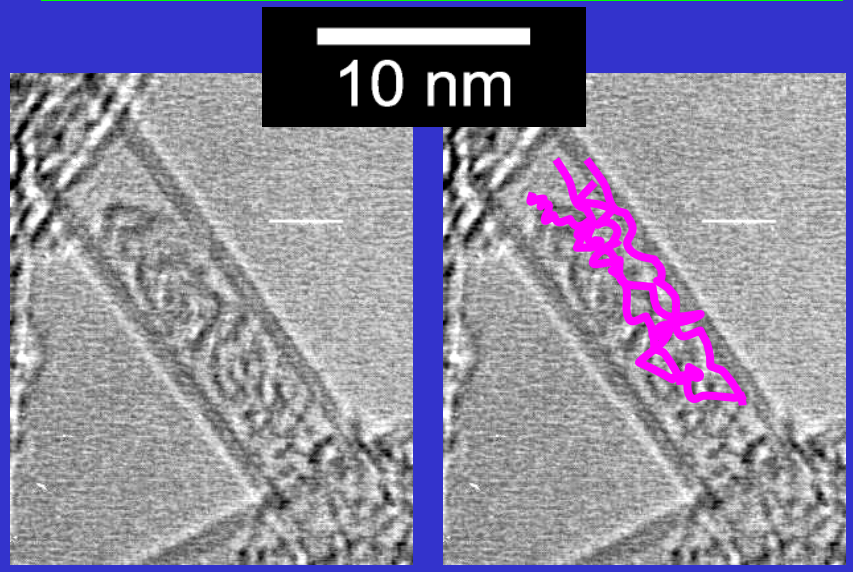
V_{RF} = 20.0 V , V_{DC} = 10.0 V , Time= 10 min.

- **The length of encapsulated materials corresponds to that of DNA used in the electrolyte plasma.**
- **The DNA encapsulation (DNA@SWNTs) is demonstrated (A_{15}-A_{45}) .**

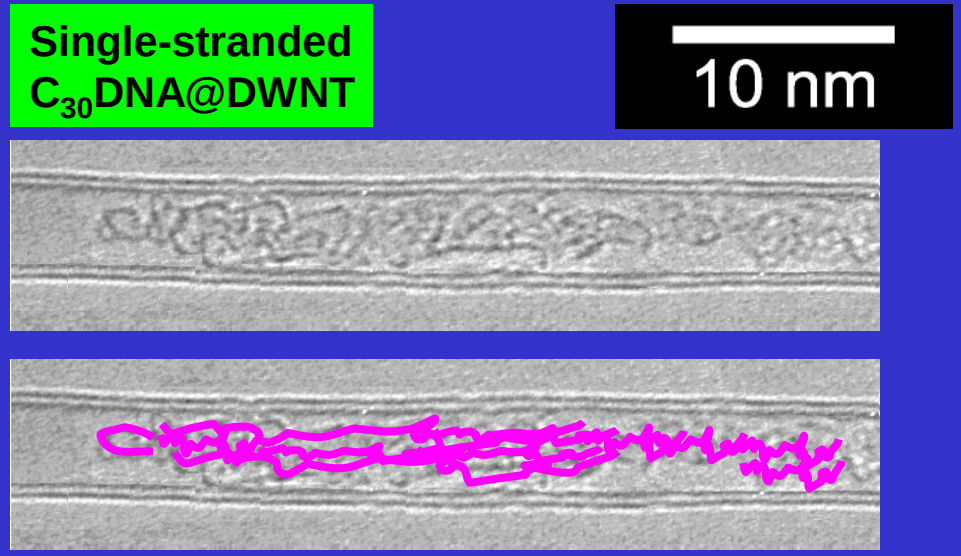
Chem. Phys. Lett. 417 (2006) 288; Jpn. J. Appl. Phys. 45 (2006) 8335

TEM Observation/Analysis : DWNTs

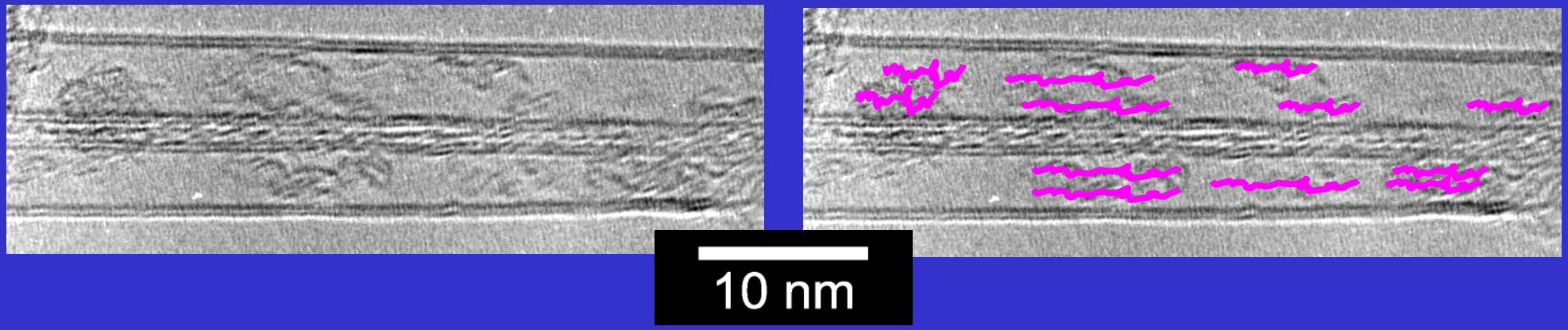
Single-stranded : G_{30}DNA@DWNT



Single-stranded C_{30}DNA@DWNT



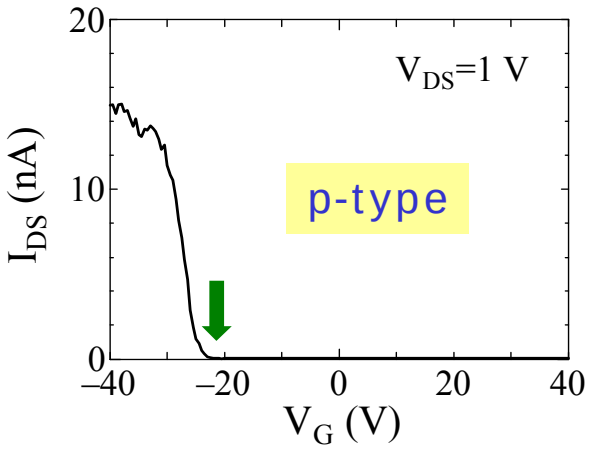
Double-stranded : G_{30}/C_{30}DNA@DWNT



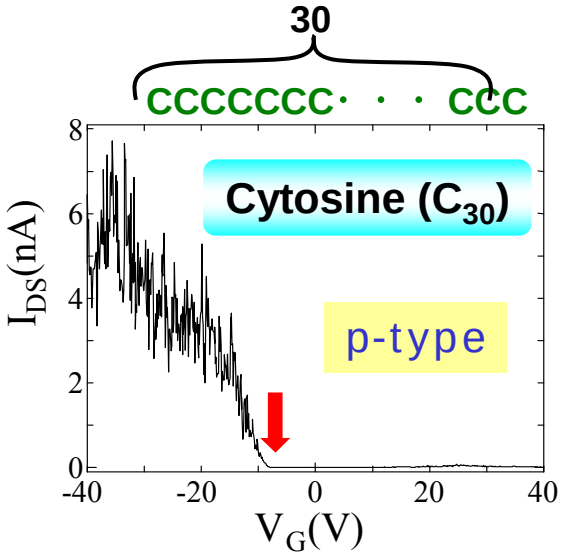
V_{DC} = 10.0 V , Time= 10 min.

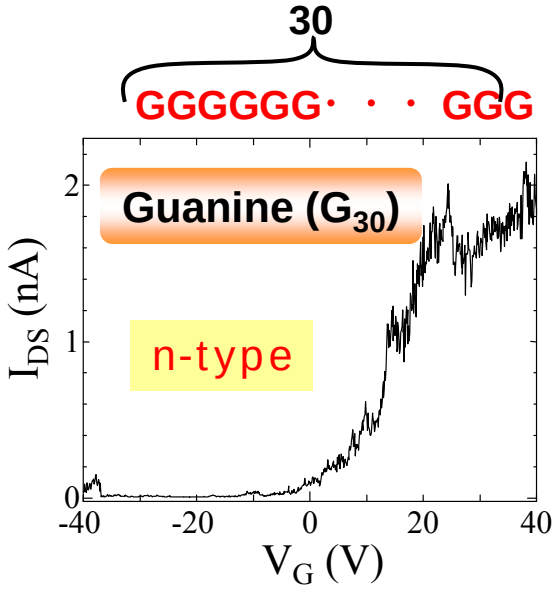
Electrical Properties of DNA Encapsulated SWNTs

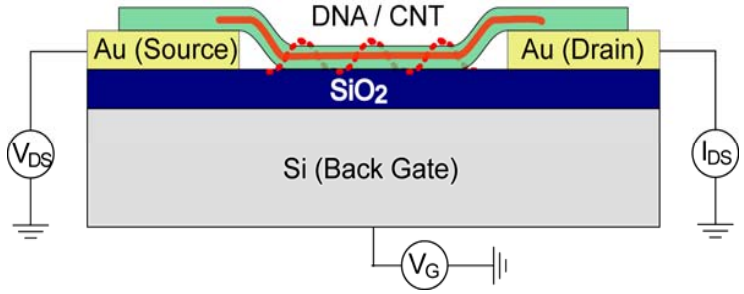
Pristine SWNTs



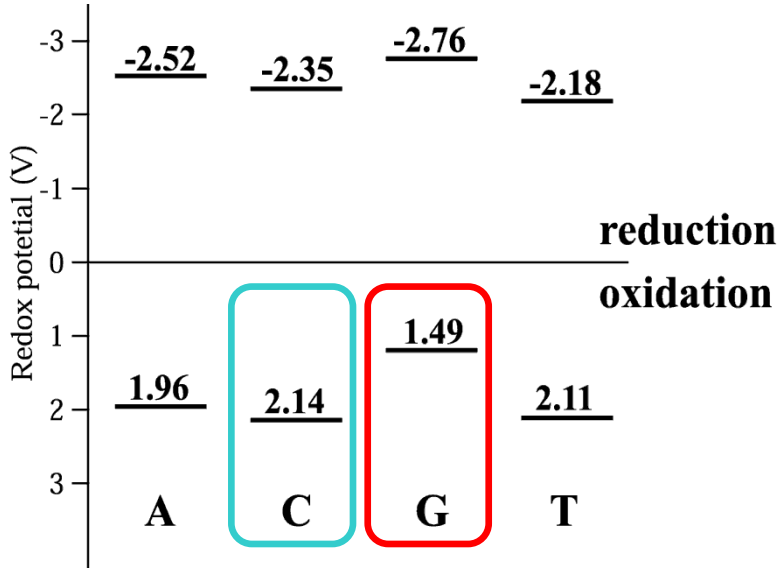
DNA@SWNTs



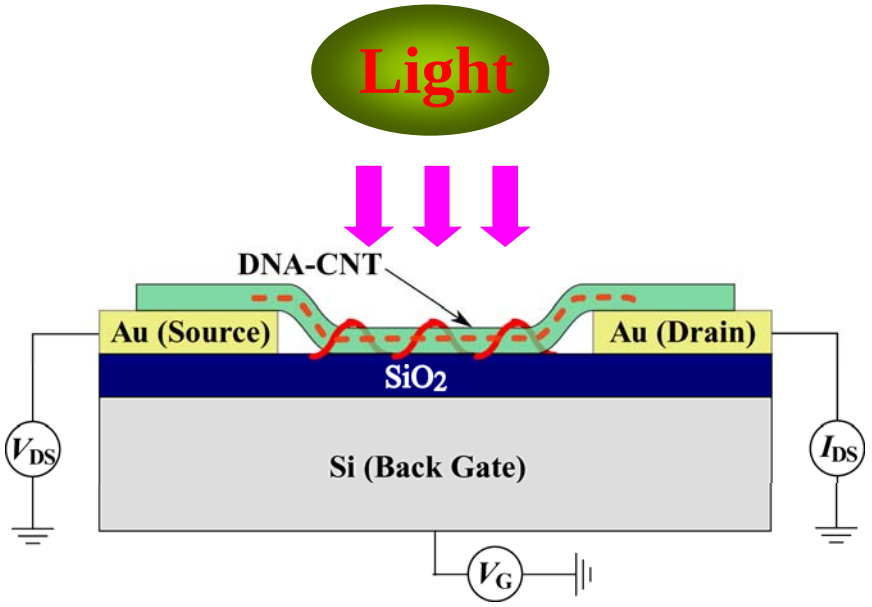




Field Effect Transistor (FET)



Light Illumination Effects on DNA Irradiated SWNTs



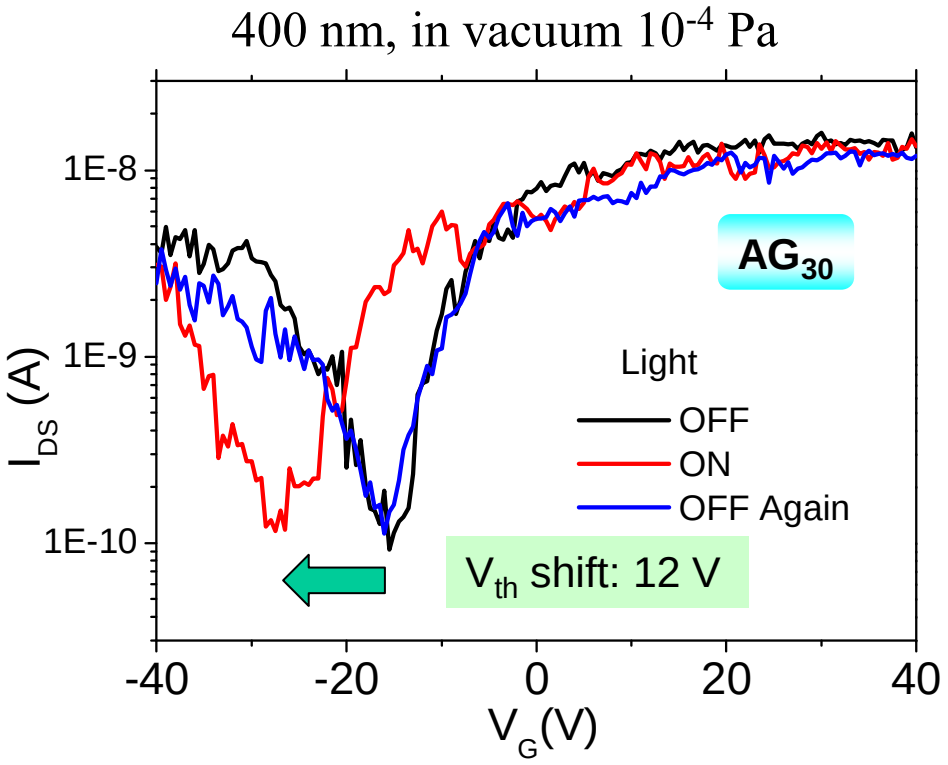
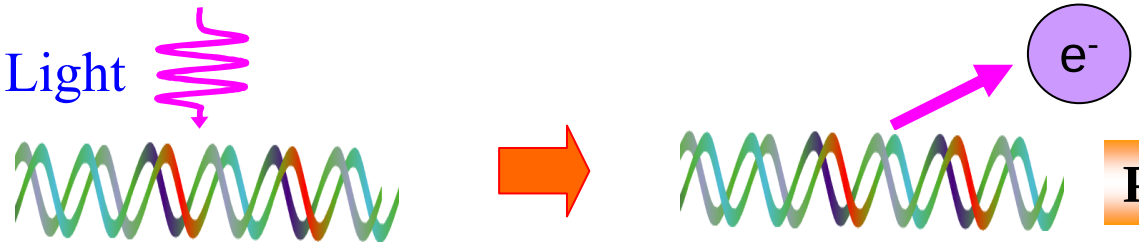


Photo induced electron transfer process



DNA in ground state **DNA in excited state**

Photo Switching Nanobio Device

3. - Liquid-Gas Interface -

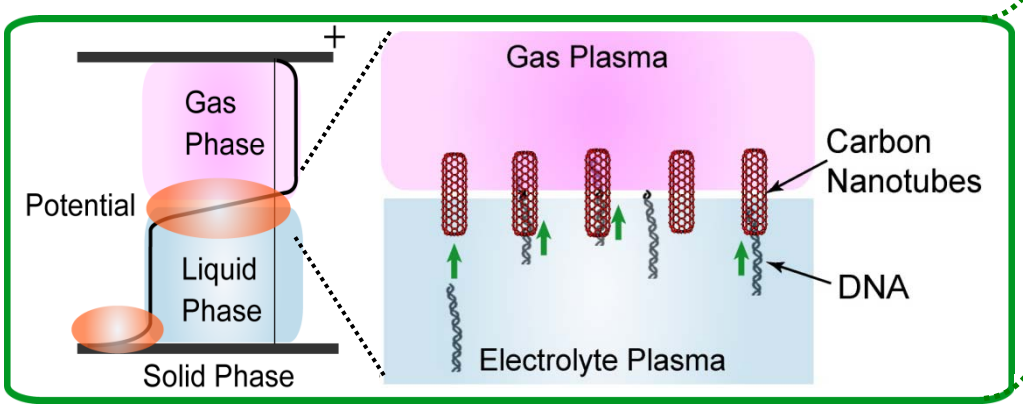
Innovating Liquid-Gas Interfacial Plasmas

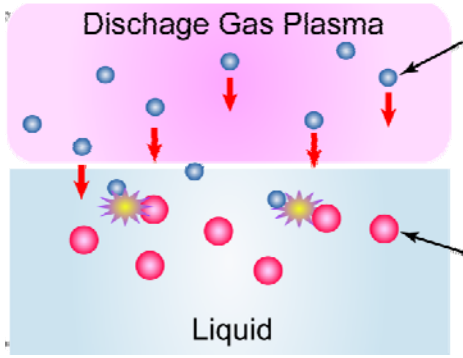
– **Novel Charged Medium** –

looking for a unique plasma-physics field

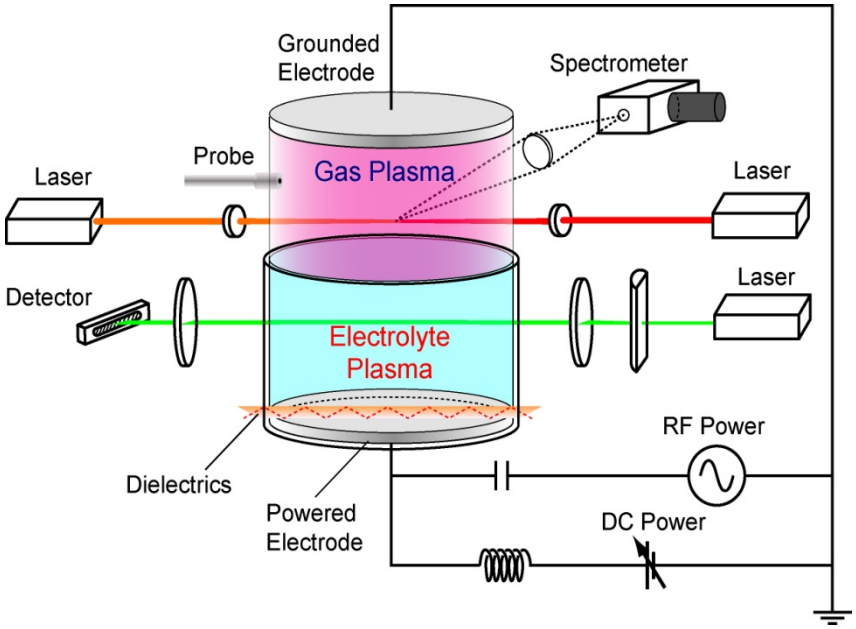
Gas-Liquid Interfacial Discharge Plasmas for Bio/Nano Applications

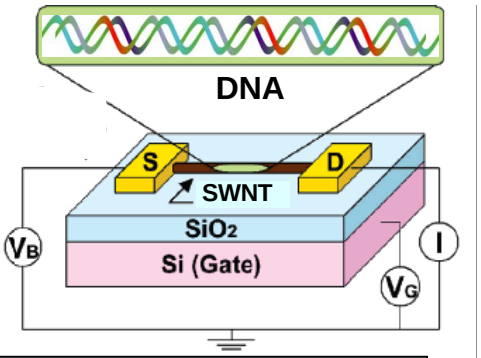
TOHOKU UNIVERSITY



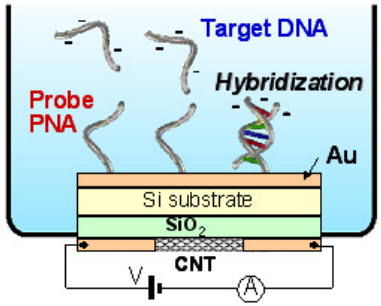


Metal Nanoparticle Synthesis

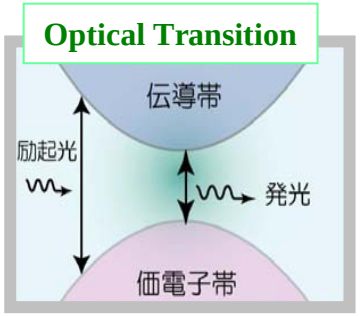




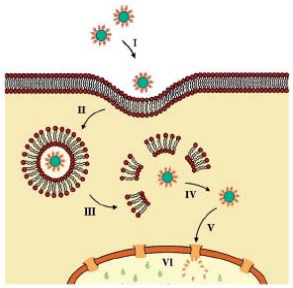
Photoelectronic Devices



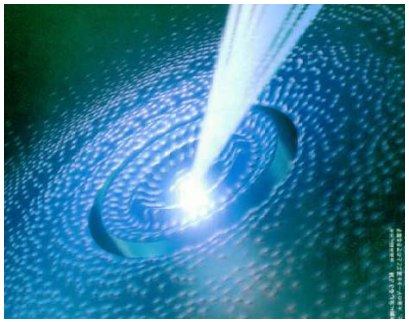
Bio Sensor



Semiconductor Optics



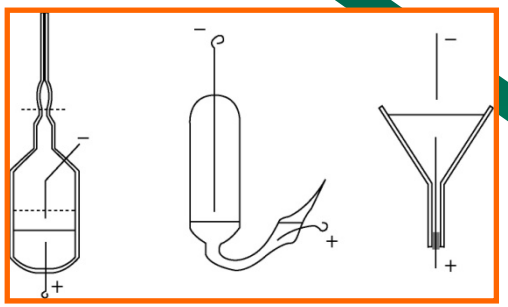
Drug Delivery



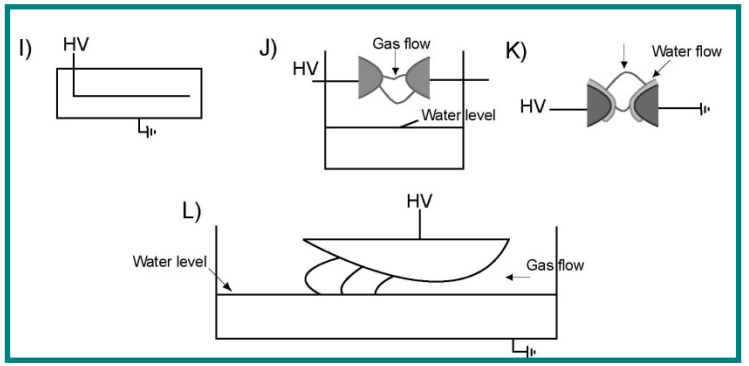
Plasmonics Therapy

History of Liquid Phase Plasmas

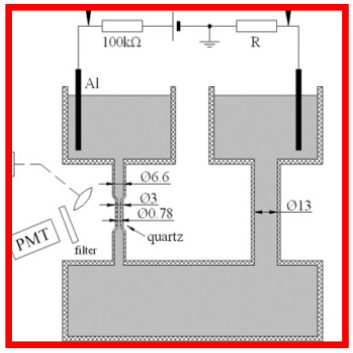
1887 ~ J. Gubkin



1923 ~ P. Debye &
E. Huckel
(Electrolyte Theory)



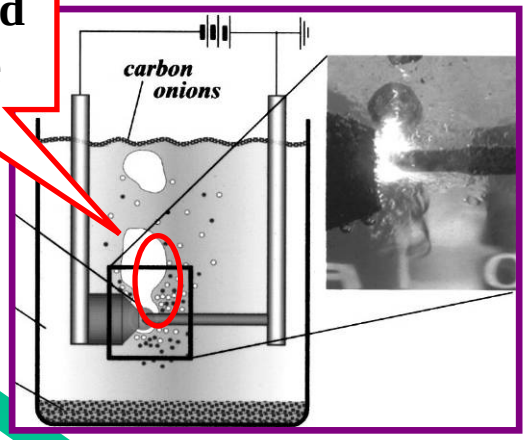
1993 ~ B. R. Locke



2001 ~ N. Sano

2002 ~ C. Lay

Gas-Liquid Interface

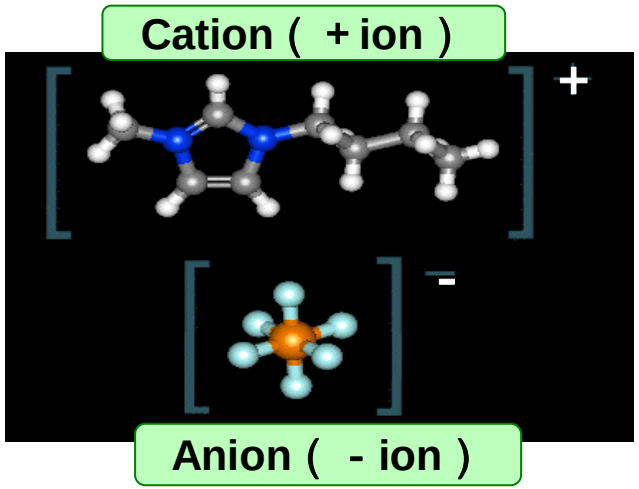


- Discharge in gas bubble generated in liquid
  ⇒ Gas – Liquid Interface is important

Fundamental Research on Liquid Phase Plasma

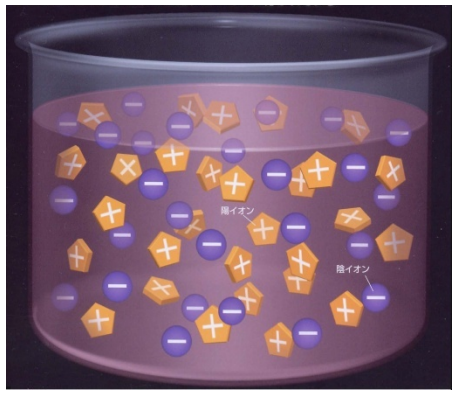
Generation of Static Gas-Liquid Interface is necessary

Ionic liquids : *dissociated into ions at room temper. w/o solvent*



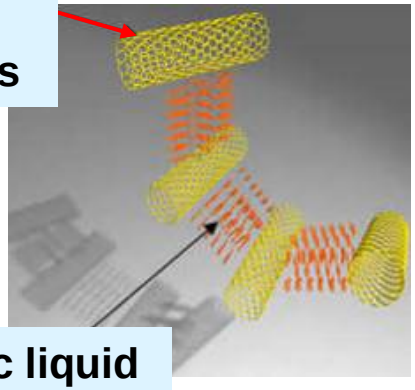
Ex. 1-butyl-3-methylimidazolium hexafluorophosphate

$[C_8H_{15}N_2]^+$ $[PF_6^-]$

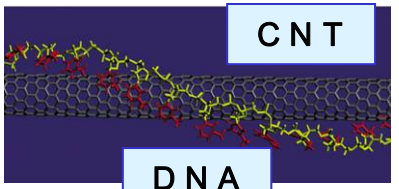


Fully ionized plasma

Carbon nanotubes



Ionic liquid



Combination of other materials

Only positive and negative ions

Extremely-low vapor pressure

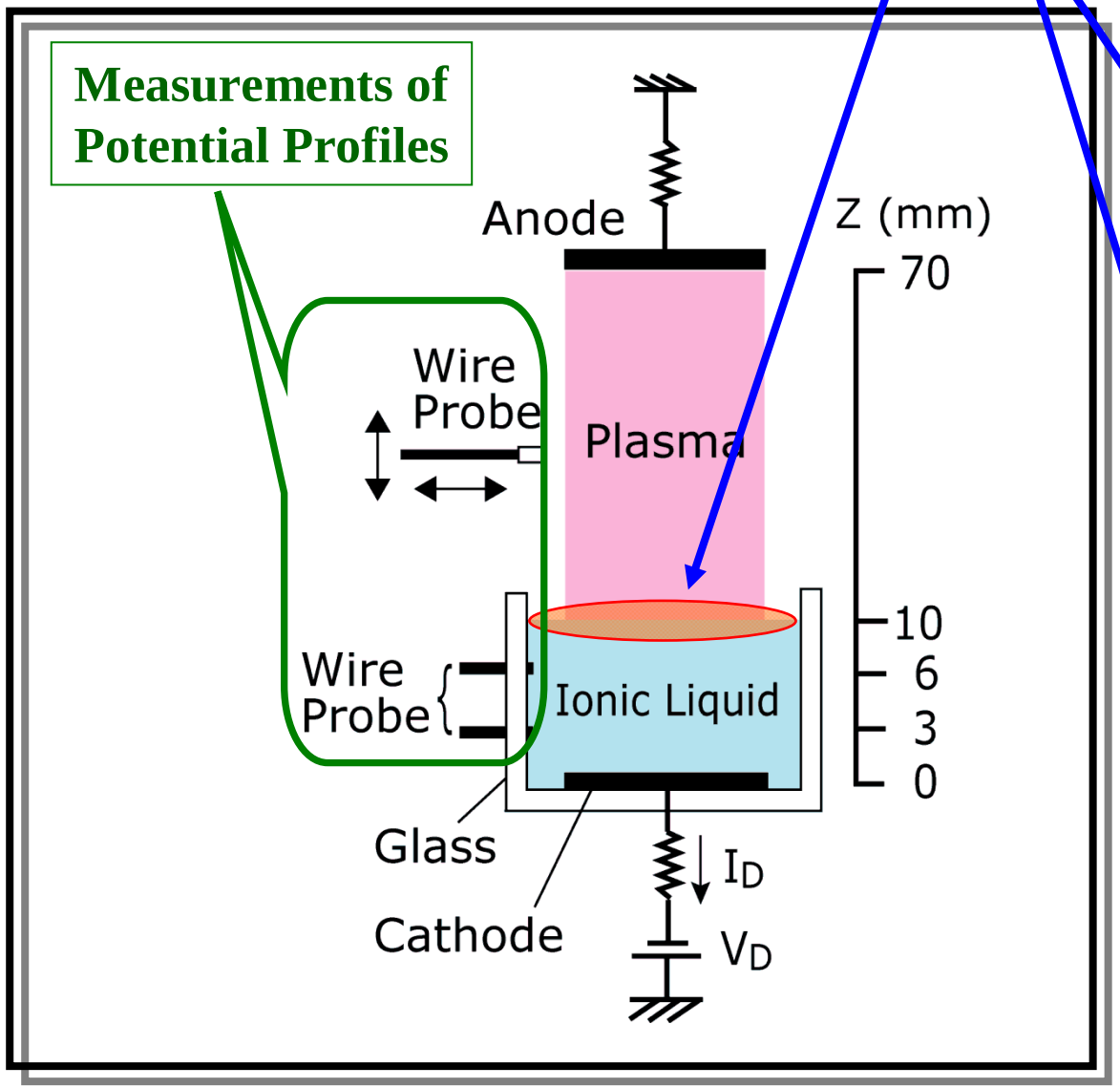
High heat capacity
Nonflammability

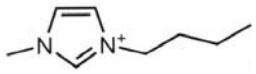
Introduction to vacuum

Stability for plasma generation

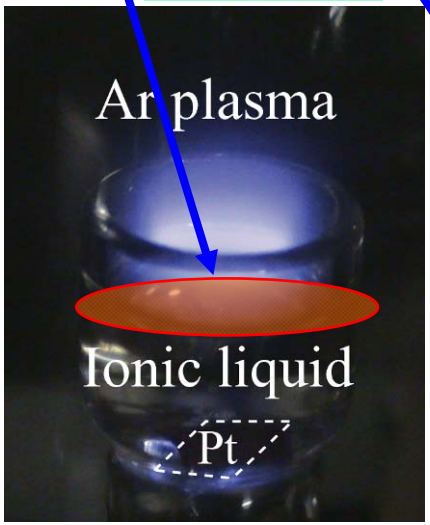
Experimental Apparatus

Static Gas-Liquid Interface

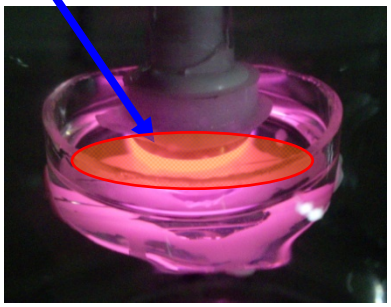


DC voltage V_{DC}	≦ 1kV
Pressure p	40 – 10^5 Pa
Gas	Ar, H_2
Discharge Gap	60 mm
Cathode Electrode	Platinum (ϕ15 mm)
Anode Electrode	SUS (ϕ15mm)
Ionic Liquid	Cation $[C_8H_{15}N_2]^+$ Anion $[BF_4]^-$ 

Low pressure



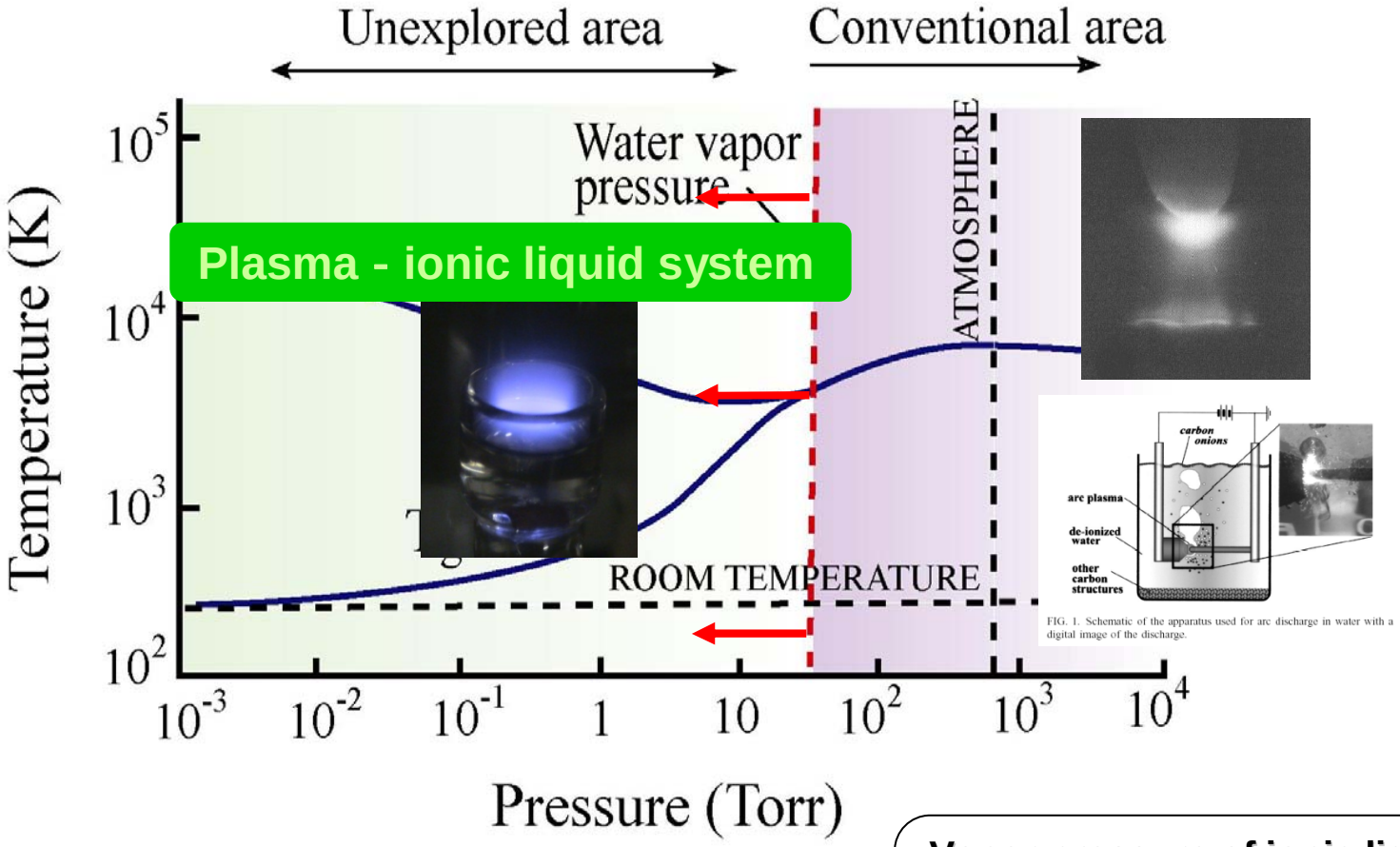
Atmospheric pressure



Appl. Phys. Lett. **90** (2007) 201501

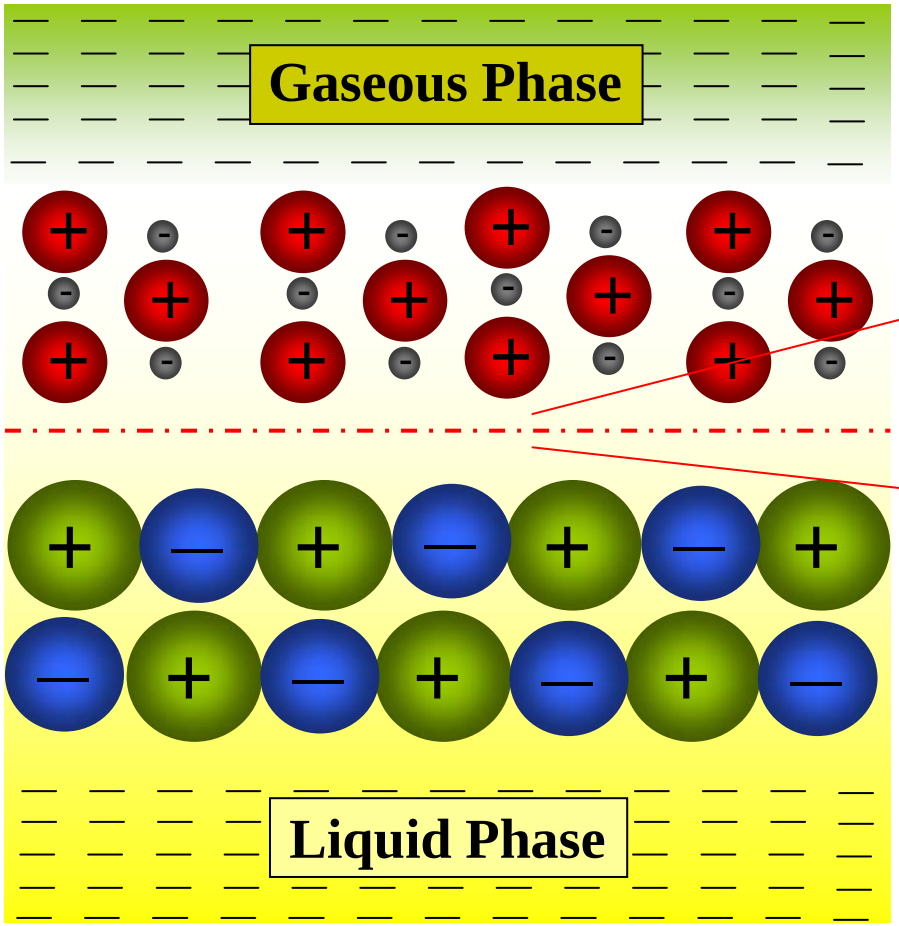
Expansion of Gas-Pressure Range in Production of Gas-Liquid Interfacial Plasmas

Operation Range of Pressure



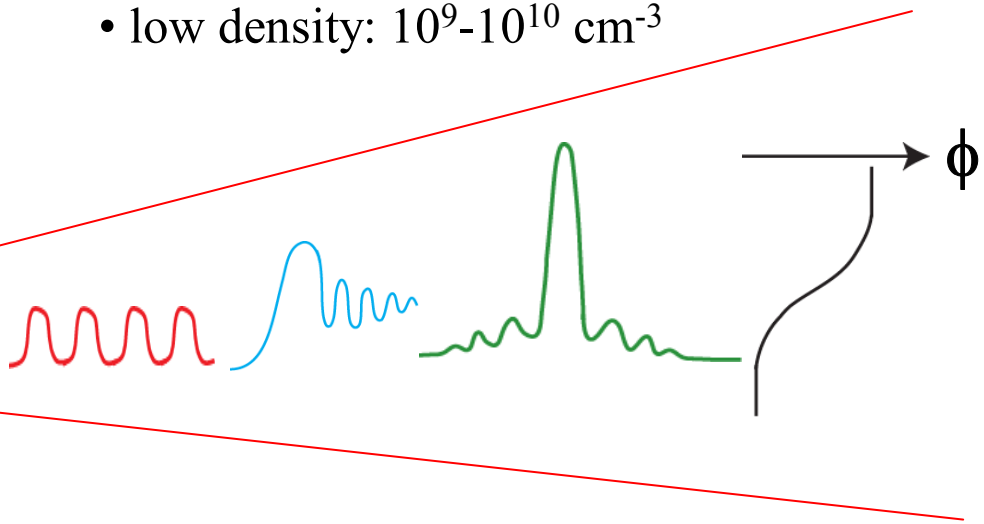
Vapor pressure of ionic liquid P_v (at 300K) :
below 10^{-2} Pa (our experimental)
below 10^{-6} ~ 10^{-7} Pa (T E M observation)

Liquid-Gas Interfacial Plasmas – Novel Charged Medium



Normal Electron-Ion Plasma

- $m_+/m_e \approx 73000$ (Ar plasma)
- low density: 10^9-10^{10} cm^{-3}

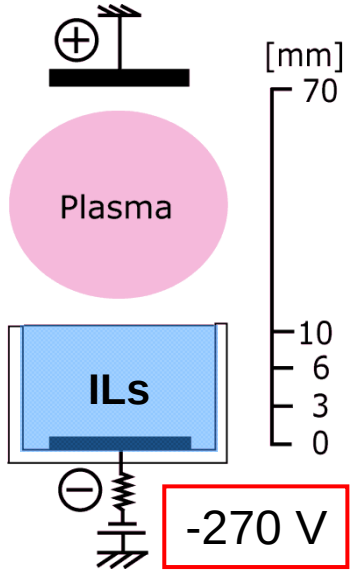


Quasipair Ion Plasma

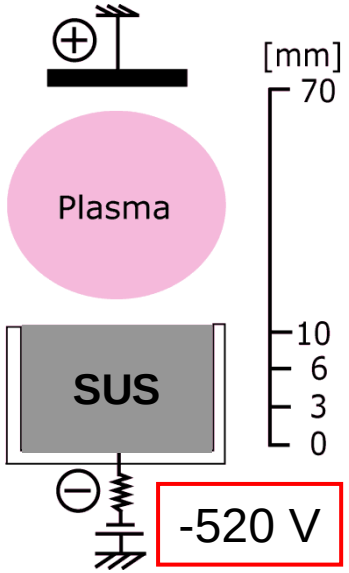
- very heavy molecule ions:
  $m_+/m_- \approx 1.6$
- high density: ~10^{21} cm^{-3}

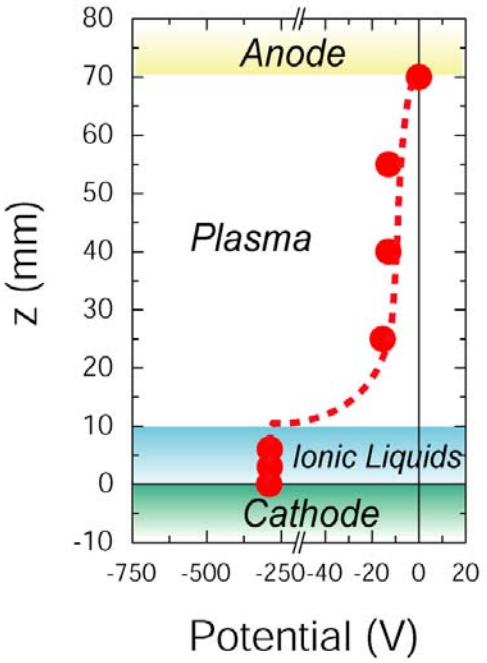
- Macroscopically stable in a sense of Rayleigh-Taylor instability
- **How about micro-stability or -structure** such as a nonlinear surface wave in the form of soliton, hole, shock, double layer, etc. ?

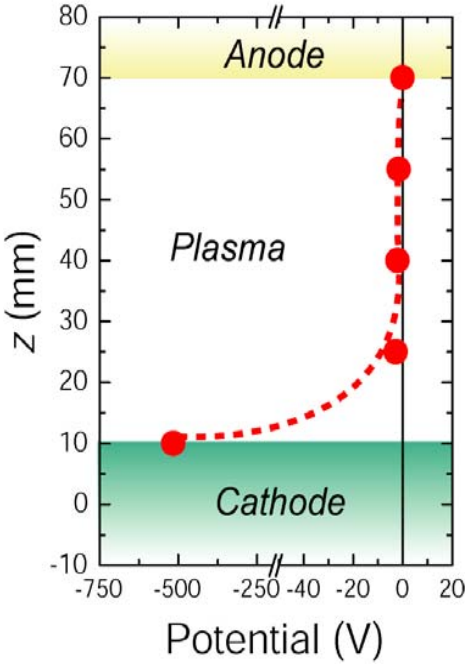
Role of Ionic Liquid as Discharge Electrode



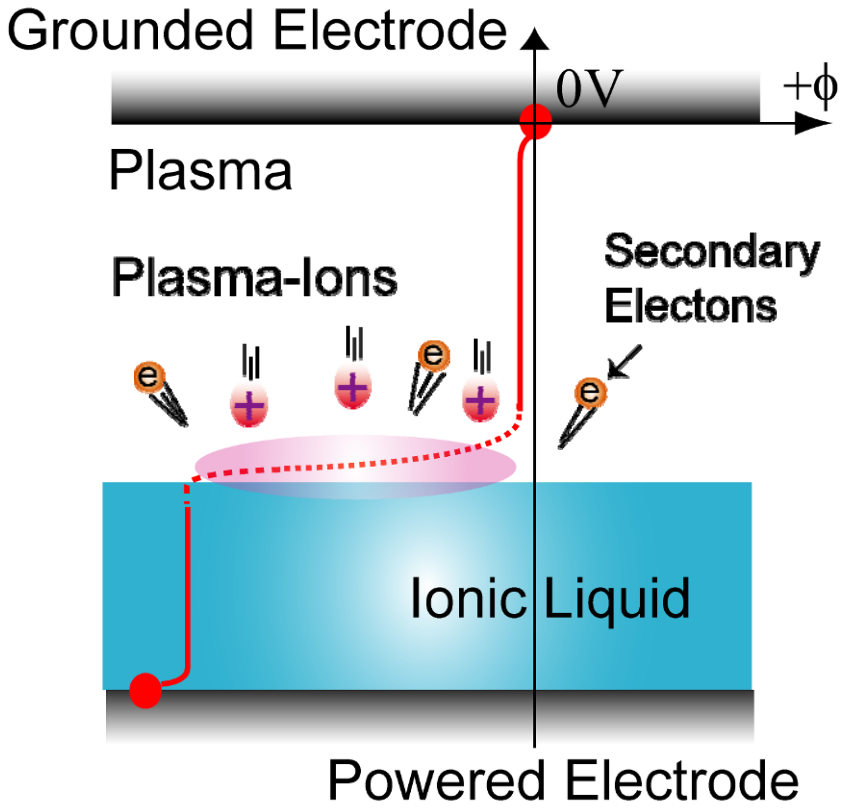
Ar Pressure: 40 Pa
Discharge Current：1 mA (Constant)

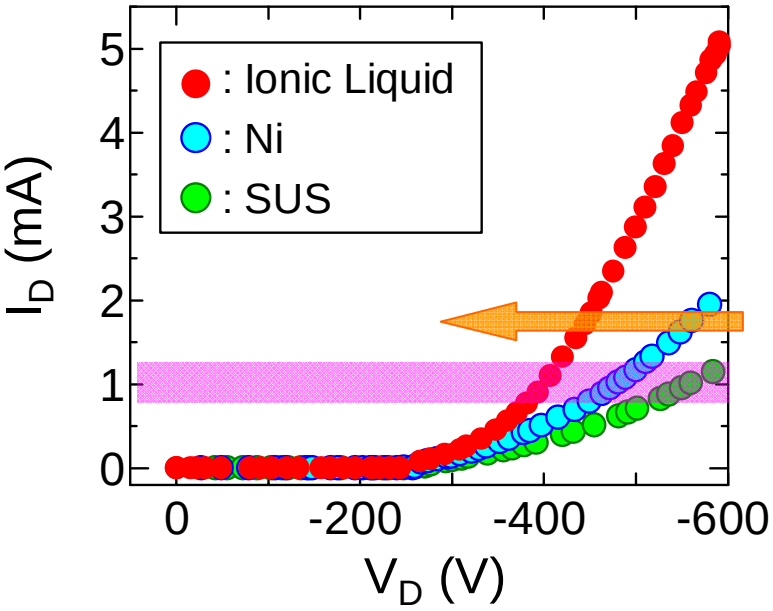






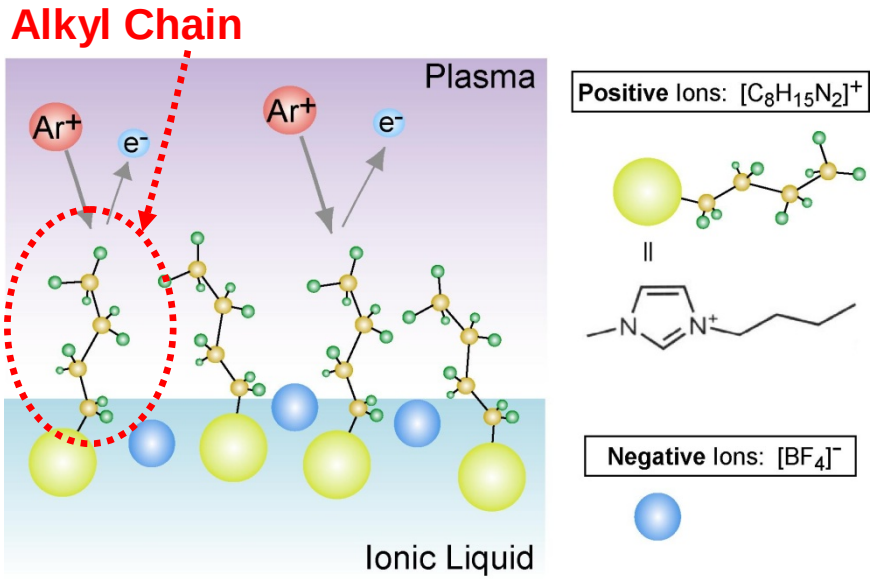
Potential Profile of Liquid-Gas Interfacial Plasma





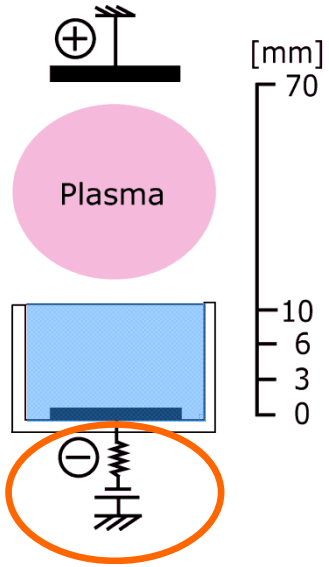
- Formation of Sheath Electric Field
- Plasma Ion Acceleration / Irradiation
- Emission of Secondary Electrons

Decrease in the Discharge Voltage

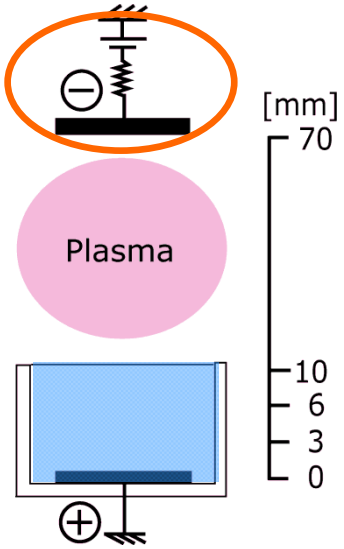


Effects of Ion Irradiation on Ionic Liquid

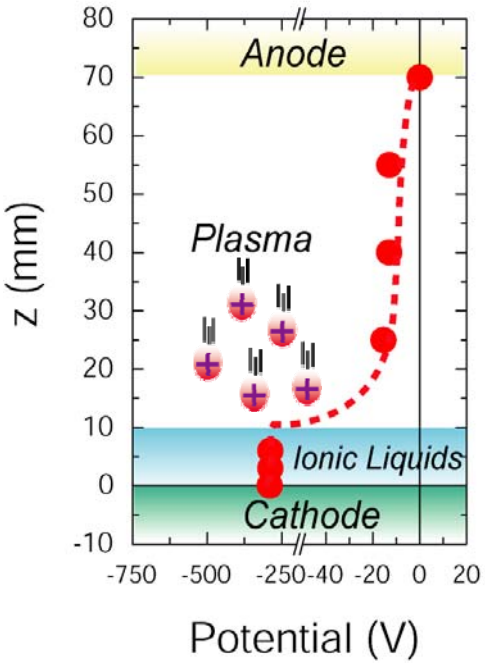
A-mode



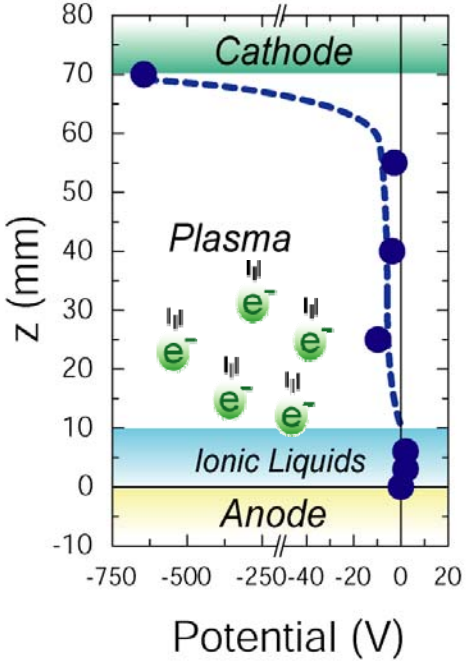
Ar Pressure: 40 Pa
Discharge Current : 1 mA (Constant)



B-mode



-300 V

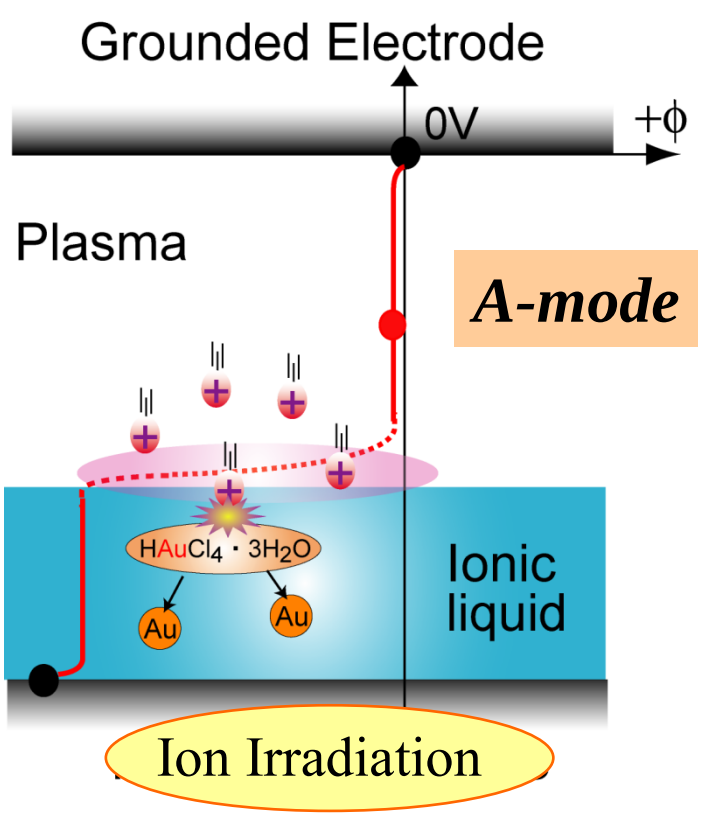


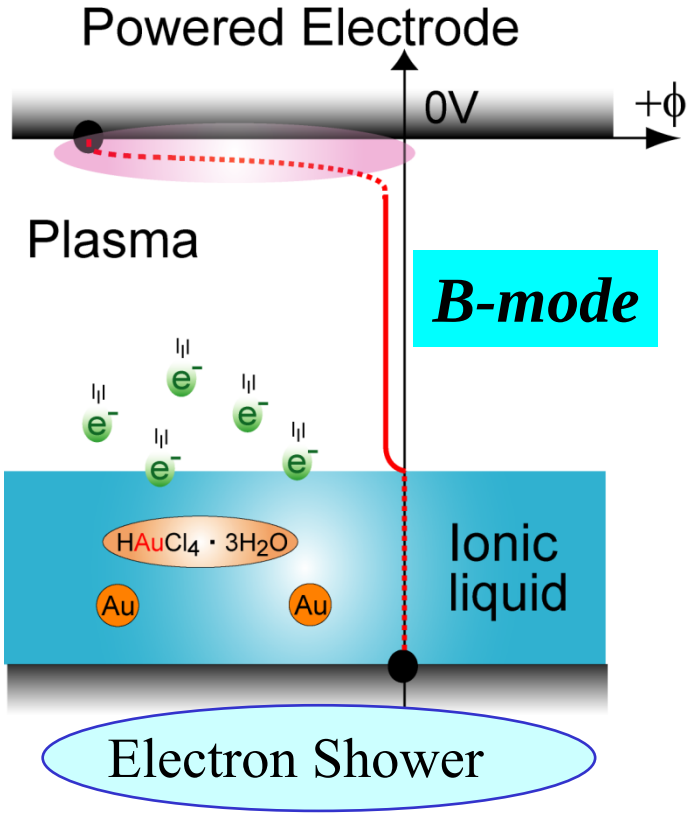
-700 V

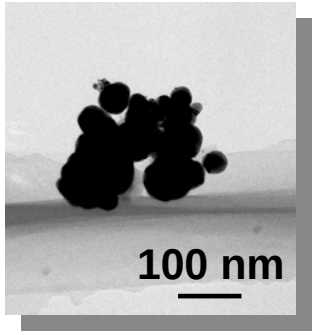
J. Appl. Phys. **105** (2009) 103306

4. Application of Liquid-Gas Interfacial Plasmas

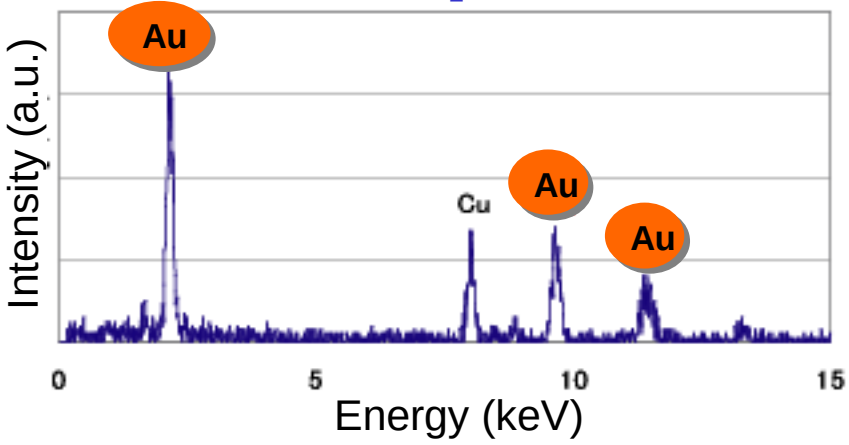
Utilization of Ion Irradiation for Nanomaterial Synthesis



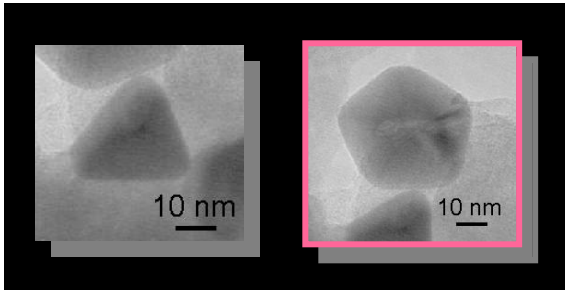




EDX Spectrum



Au Nanoparticles

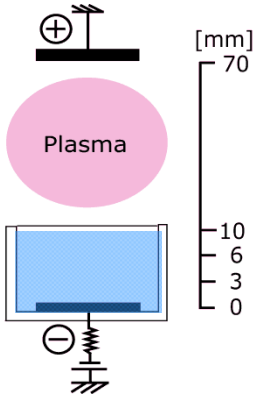


Au Nanoparticle Synthesis Using Plasma Irradiation

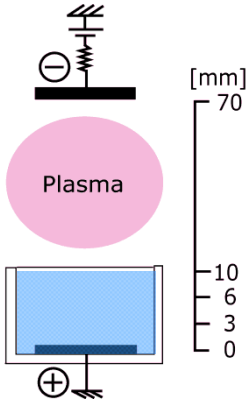
TOHOKU UNIVERSITY

A-mode

Ion Irradiation

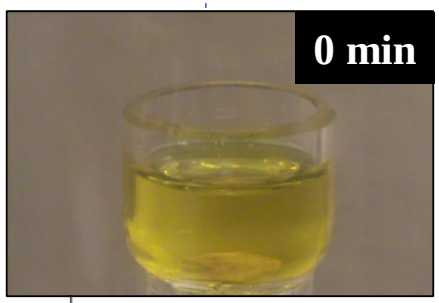


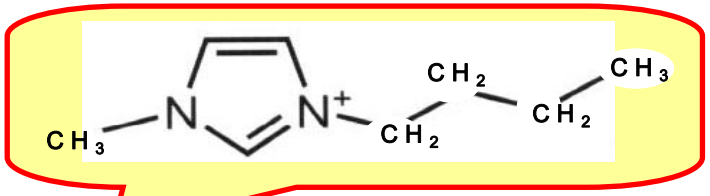
$P_{Ar} = 60$ Pa
$I_D = 1$ mA
$t = 7$ min



B-mode

Electron Shower

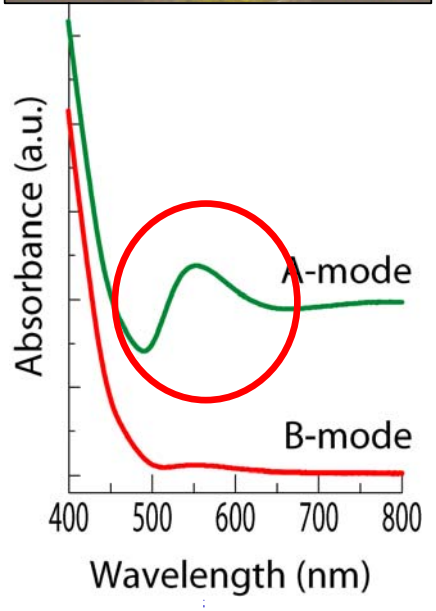




$H^* + Au^{3+} \longrightarrow H^+ + Au^{2+}$

$\vdots$

$H^* + Au^+ \longrightarrow H^+ + Au^0$



$Au^{3+} + e^- \longrightarrow Au^{2+}$

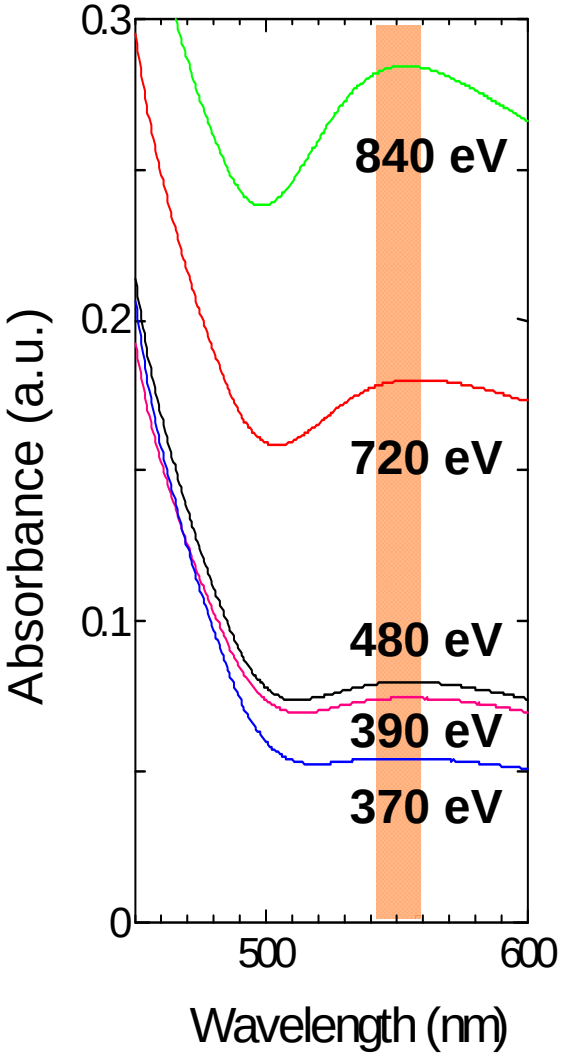
$\vdots$

$Au^+ + e^- \longrightarrow Au^0$

Appl. Phys. Express **2** (2009) 035006

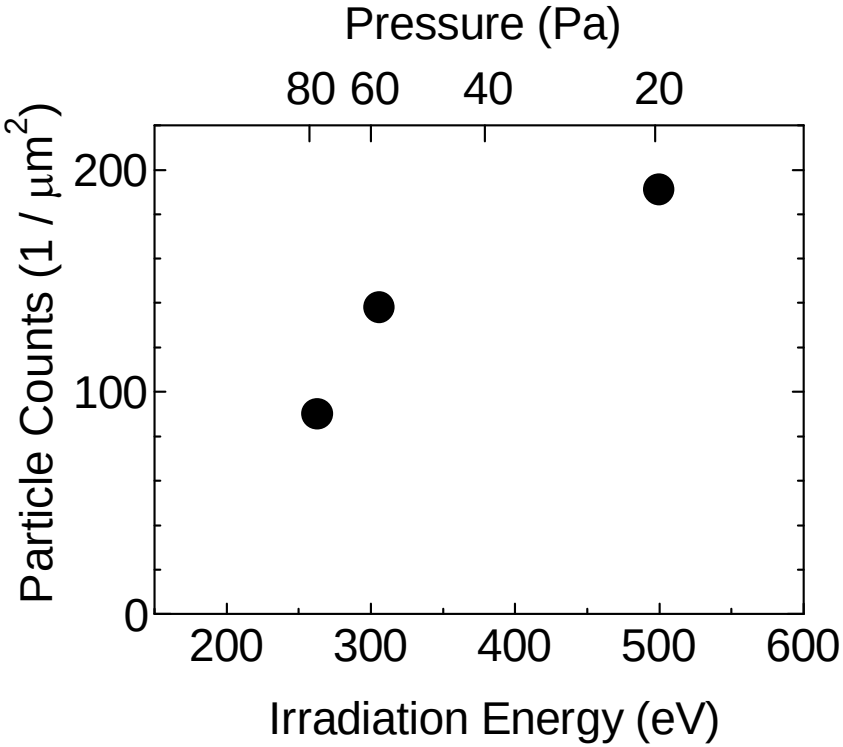
Dependence of Particle Counts on Ion Irradiation Energy

Surface Plasmon Resonance



I_D = 1 mA, A-mode

Au Nanoparticle Counts



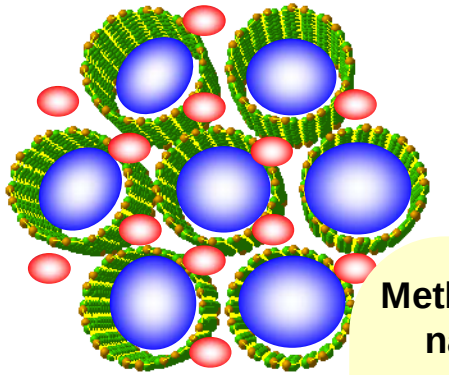
Efficiency of nanoparticle synthesis is enhanced by increase in ion irradiation energy

Application of Gas-Liquid Phases Interfacial Plasmas

~ Novel Application of gas-liquid interfacial field ~

CNTs

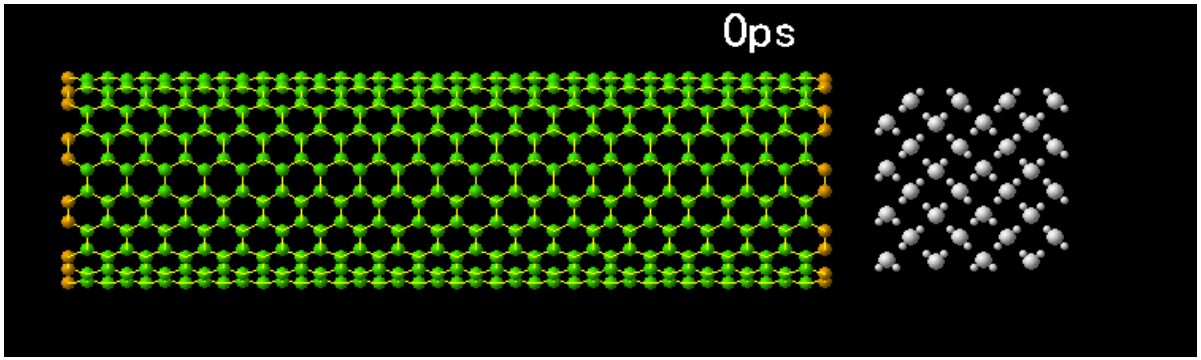
Nanospace
- Inner hollow region
- Between CNT-CNT (bundle-bundle)



CNTs Bundle

Liquid

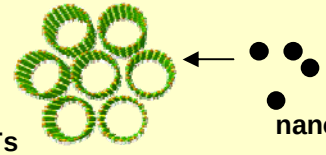
- Liquid can be introduced into any space
- Ingredients (Au ions) can directly be introduced into nanospaces

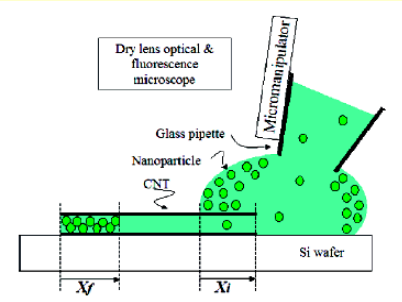


丸山研究室ホームページ (東京大学) http://www.photon.t.u-tokyo.ac.jp/index-j.html

Method of indirect-synthesis for nano- compounds creation

- ✓予め3nm 以下のナノ粒子を合成
- ✓会合手法の検討
- ✓層間挿入・・・ 不均一
- ✓直径の大きな多層CNTsに制約

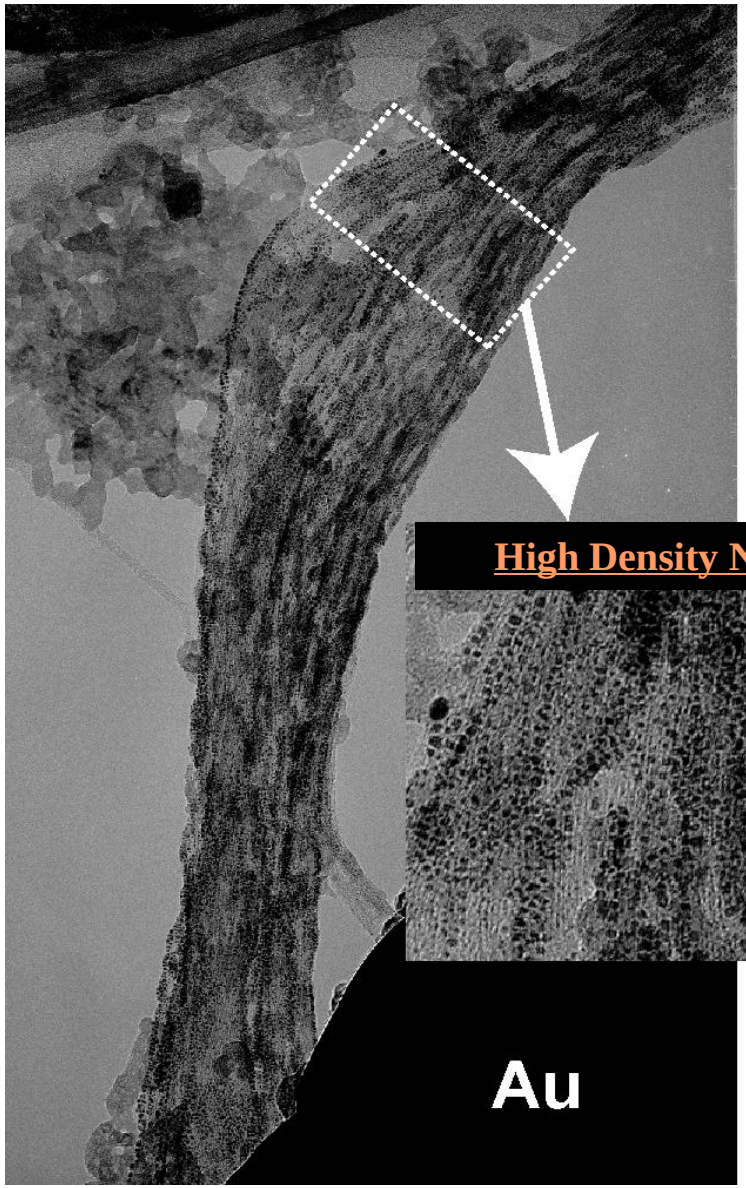


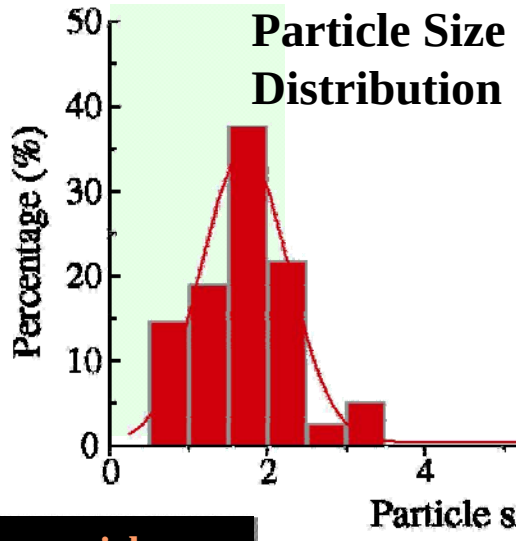


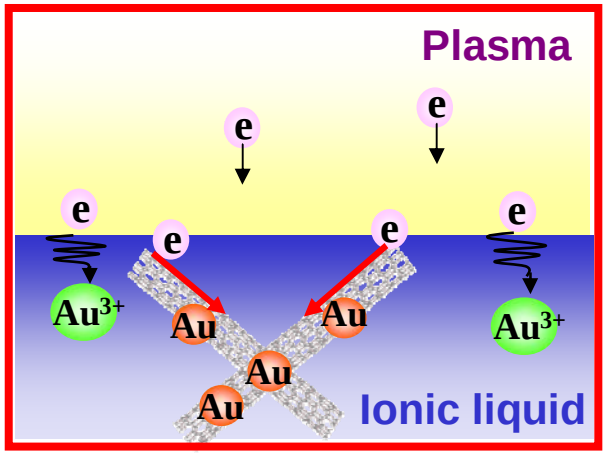
Method of direct nanoparticle-synthesis utilizing CNT nanospaces as reaction field

Synthesis of Au Nanoparticle with Carbon Nanotubes

Single-Walled Carbon Nanotubes (SWNTs) are used as a template.

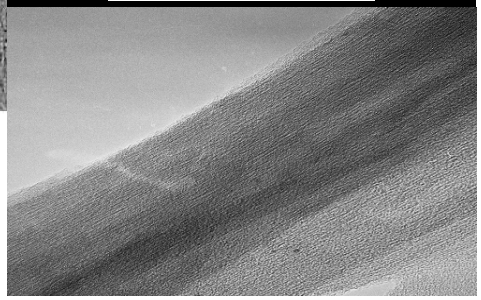






High Density Nanoparticles

SWNT Bundles



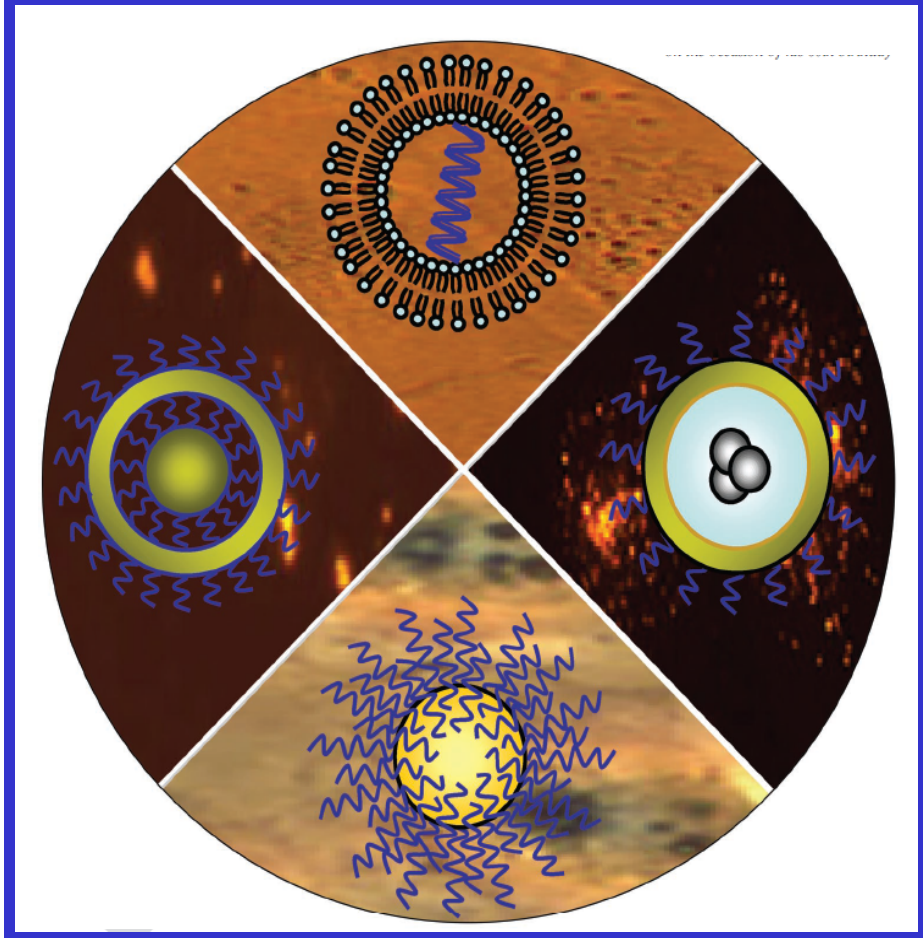
- ✓Small Size < 2 nm
- ✓High Density
- ✓Monodispersed

SWNTs with unique Electrical / Magnetic / Optical Properties

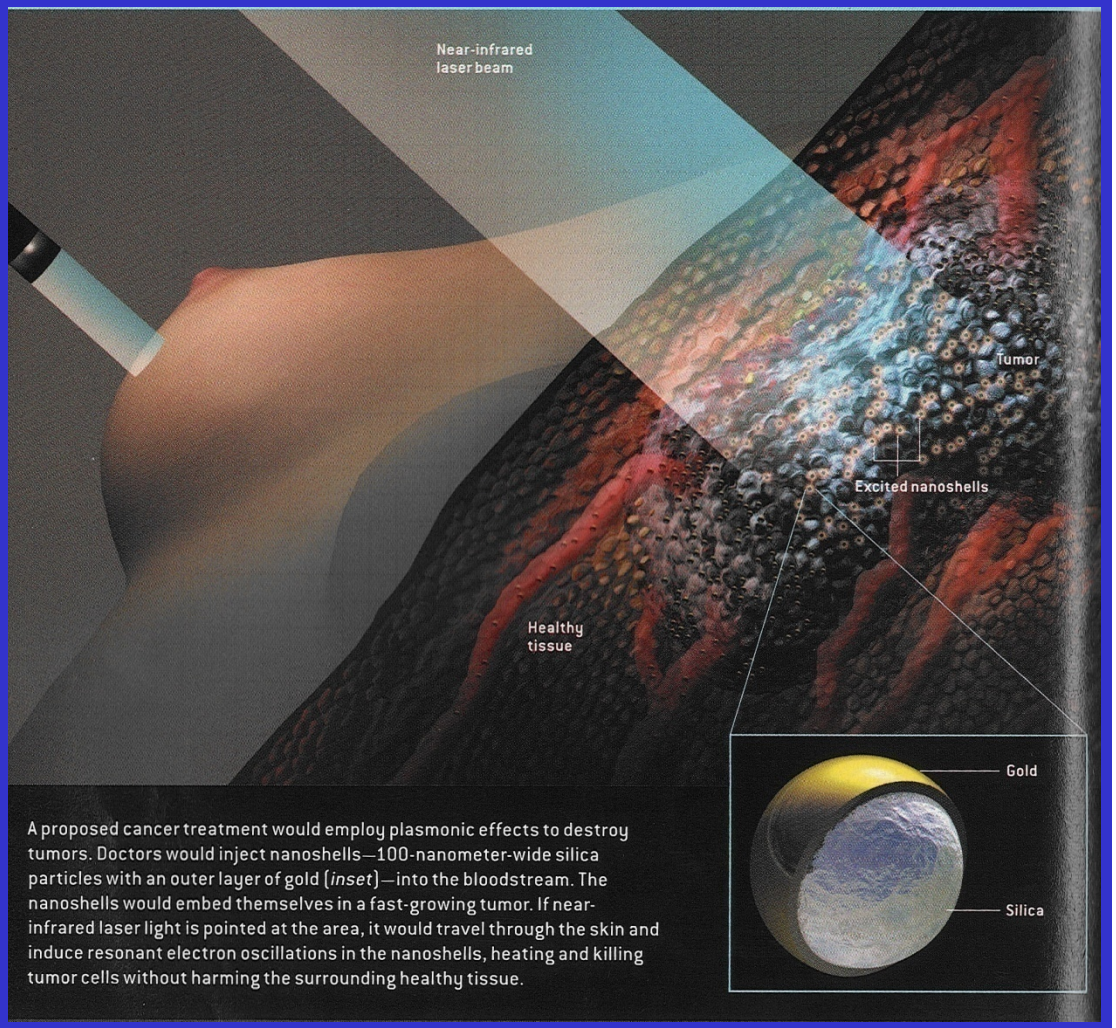
10 nm

The Next Generation Nanoparticle Technology Illuminating Bio/Medicine World

Drug Delivery System



Plasmonic Therapy for Cancer



A proposed cancer treatment would employ plasmonic effects to destroy tumors. Doctors would inject nanoshells—100-nanometer-wide silica particles with an outer layer of gold (*inset*)—into the bloodstream. The nanoshells would embed themselves in a fast-growing tumor. If near-infrared laser light is pointed at the area, it would travel through the skin and induce resonant electron oscillations in the nanoshells, heating and killing tumor cells without harming the surrounding healthy tissue.

Summary

Liquid-gas-solid interfacial plasmas are investigated for the purpose of looking for a unique plasma-physics field and applying fundamental physics to nano and bio sciences.

DNA Control in Electrolyte Plasmas

- ✓ Effects of electric fields on ion irradiation in electrolyte plasmas are clarified, and DNA encapsulated carbon nanotubes (SWNTs, DWNTs) are effectively created.
- ✓ Their electronic transport properties are demonstrated to be modified depending on the kinds of DNA irradiated to the carbon nanotubes, which are expected to be applied to bio/nano photoelectronic and nanomedicine systems.

Generation of Static Gas-Liquid Interfacial Plasmas – Novel Charged Medium –

- ✓ The generation of stable discharge plasmas in contact with ionic liquid is surprisingly achieved in the range of both atmospheric and low gas pressures.
- ✓ The large potential difference (sheath electric field, double layer) is found to be formed in the gas-liquid interfacial region and causes ion irradiation toward the ionic liquid, which could contribute to the effective creation of nano-composite materials in the ionic liquid incorporated discharge plasmas.
- ✓ Are there any interesting phenomena on waves and instabilities such as a nonlinear surface wave in interfacial regions, which are sandwiched between normal electron-ion gaseous plasmas and quasipair molecule-ion liquid plasmas ?