東京大学 大学院理学系研究科 山野井 慶徳

シアノバクテリアの光化学系Iを活用した電極の作製と物性評価

研究概要

本研究では、光合成タンパク質複合体の高い光電変換能を最大限に利用するため、これらのタンパク質と微小電極を組み合わせた光センサを構築した。具体的には、グラフェンFET上に金ナノ粒子と光化学系Iを固定化し、グラフェンの*I-V*特性変化から光を検出する手法について研究を行った。まずグラフェン上にナノ粒子と光化学系Iを固定化する最適条件を見出した。続いてグラフェンFET上にこれらを固定化し、励起光照射下での*I-V*特性を調査した。

今後の展望

研究結果をもとに、最終的には微小電極上に1つの光化学系Iを固定化し、電圧測定によって単電子移動を観測することを目指している。電気化学測定によって単電子移動を捉えられれば、生体分子を用いた単光子検出システムとして、学術上、応用上ともに重要な成果となる。

現在は、グラフェンFET上の金ナノ粒子と光化学系Iを用いて微弱光の検出を目指している。本研究を通して、グラフェンを用いた光検知という新たな研究領域を開拓できる。

Photosystems - Key proteins in photosynthesis

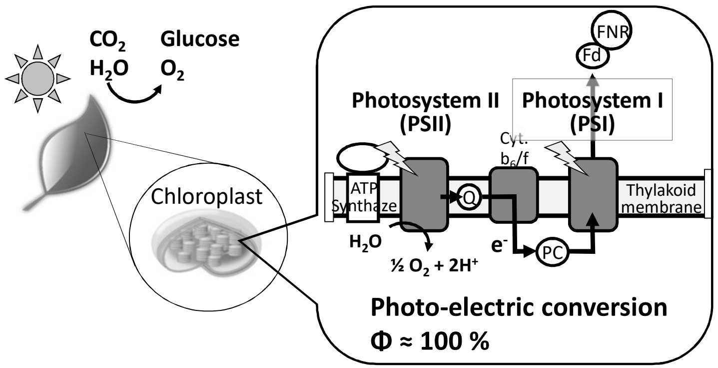
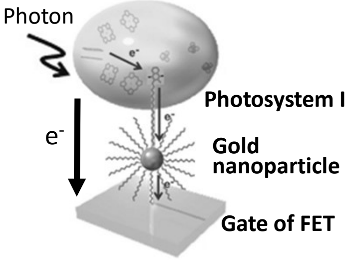


Photo-electric conversion
Φ ≈ 100 %

Photosystems are promising materials for new light sensing devices.

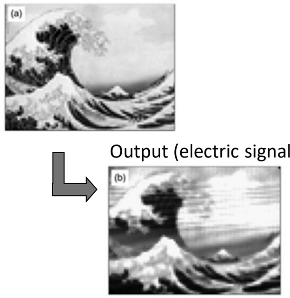
Previous research on PSI

"Bio-photosensor" invented by our research group



Terasaki, N. Hiraga, T. Inoue, Y. Nishihara, H. Minakata, M. Fujii, M. et al. *Biochimica et Biophysica Acta, Bioenergetics* **2007**, *1767*, 653-659.

Input (light signal)

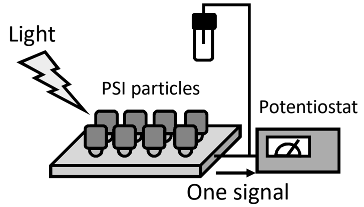


Output (electric signals)

PSI = New material for light sensors

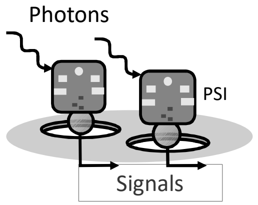
Development of the previous research

Previous system



- The electrode was large.
- A large number of photons
  → One signal

Ideal system

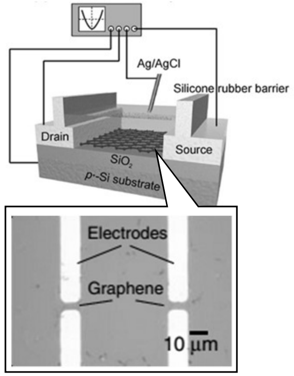


- The electrode is small.
- One single photon
  → One signal

Use a small electrode to fabricate the light sensor
→ Convert every single photon into an electric signal

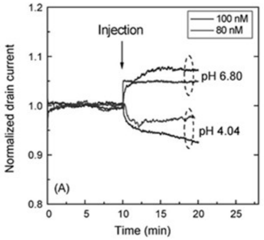
Graphene field effect transistors for sensors

Structure of graphene FETs



Zaifuddin, N. M. *et al. J. Appl. Phys.* **2013**, *52*, 06GK04-1/06GK04-4.

Change in the drain current induced by biomolecules

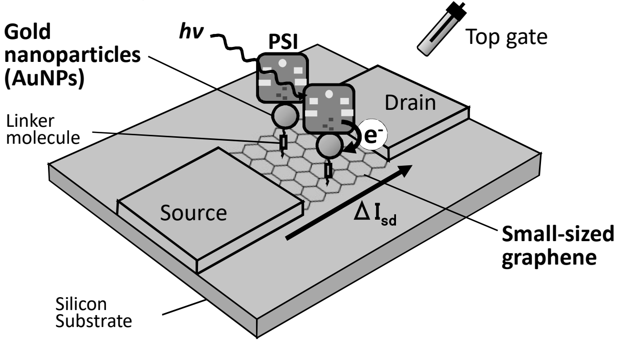


Ohno, Y. et al. Biosens. Bioelectron. 2010, 26, 1727-1730.

Highly sensitive detection of biological and chemical molecules.

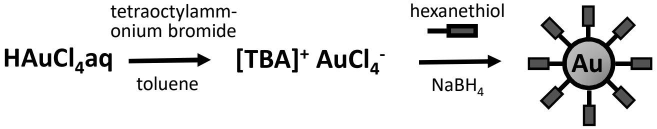
My research objective

A light sensor based on PSI, AuNPs and graphene FET for the single photon detection



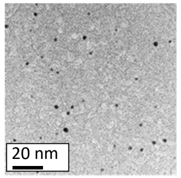
Electron transfer → Change in the source-drain current (I_{sd})

Synthesis of gold nanoparticles

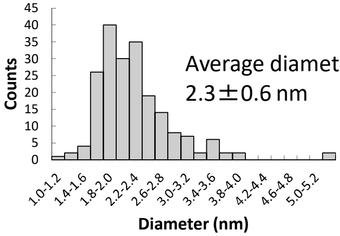


$$HAuCl_4aq \xrightarrow[\text{toluene}]{\text{tetraoctylammonium bromide}} [TBA]^+ AuCl_4^- \xrightarrow[NaBH_4]{\text{hexanethiol}} Au$$

Transmission electron microscopy (TEM) analysis



Size distribution

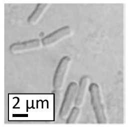


Average diameter 2.3±0.6 nm

PSI and graphene FET

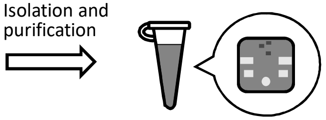
PSI : Tokyo University of Science (Prof. Tomo's lab)

T. elongatus (BP-1)

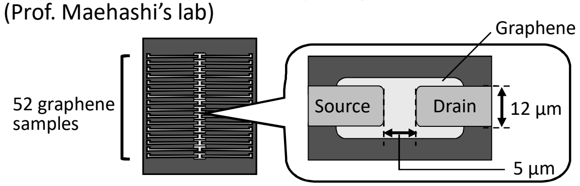


Isolation and purification

PSI in buffer solution

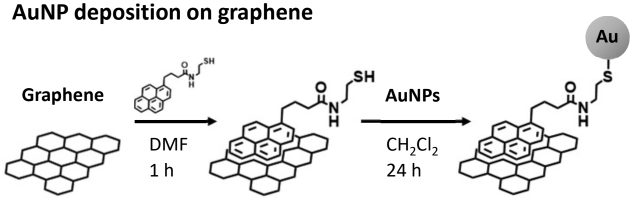


Graphene FET: Tokyo University of Agriculture and Technology (Prof. Maehashi's lab)

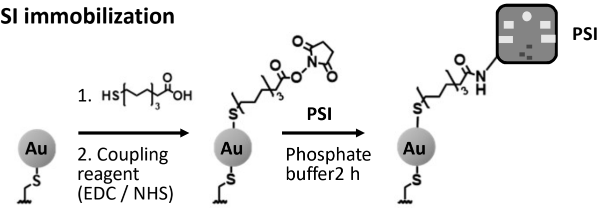


Functionalization of the electrode

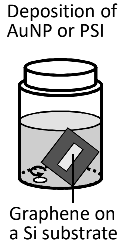
AuNP deposition on graphene



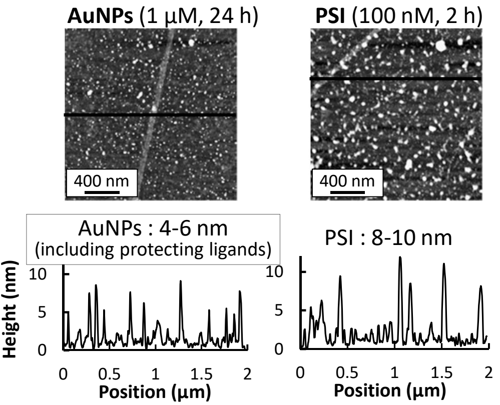
PSI immobilization



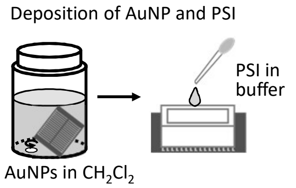
Immobilized AuNPs or PSI on graphene



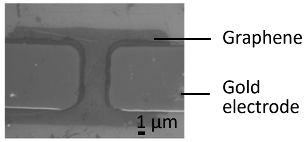
Atomic force microscopy (AFM) analysis



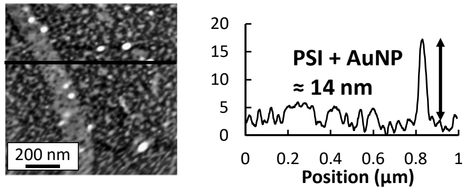
Immobilized AuNPs and PSI on a graphene FET



Scanning electron microscopy (SEM) analysis

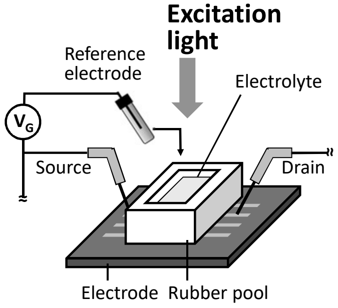


AFM image of PSI and AuNP on graphene

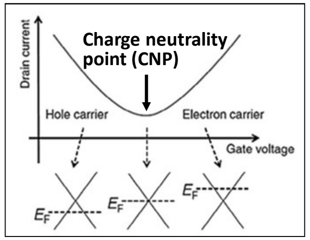


	Height
AuNPs	4-6 nm
PSI	8-10 nm

FET measurements - Experimental setup



Source-drain current (I_{sd}) against Gate voltage (V_G)



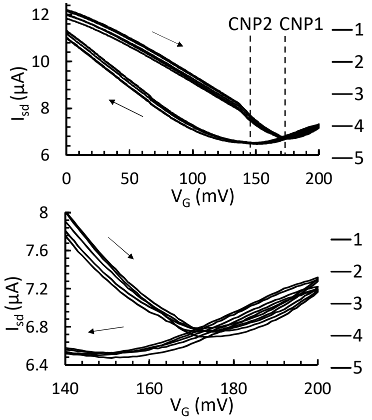
Tran, T.-T.; Mulchandani, A. *Trends in Analytical Chemistry* **2016**, *79*, 222-232.

Electrolyte:
100 mM $NaClO_4$, 250 mM NaAsc, 2.5 mM DCIP, 20 mM MES (pH 6.4)

Illumination of excitation light
→ Charge transfer (PSI/AuNPs)
→ Shifts in CNPs

FET measurements - Results

Source-drain current under illumination



1: dark
2: 680 nm Intensity = 20%
3: 440 nm Intensity = 20%
4: 440 nm Intensity = 40%
5: dark

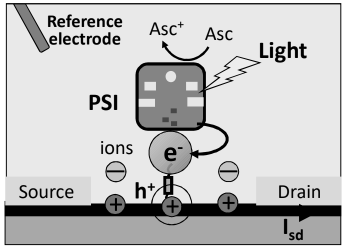
	CNP1	CNP2
1	+ 172 mV	+ 146 mV
2	+ 172 mV	+ 146 mV
3	+ 174 mV	+ 150 mV
4	+ 175 mV	+ 150 mV
5	+ 174 mV	+ 152 mV

+2 mV
+4 mV

Blue light irradiation
→ h^+ doping of graphene

Mechanisms of the hole doping effect

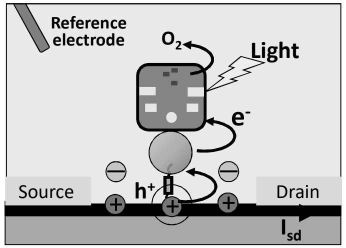
Mechanism 1 : Gating effect



e.g. Charged proteins adsorbed on the graphene FET

Kim, J. E.; No, Y. H.; Kim, J. N.; Shin, Y. S.; Kang, W. T.; Kim. Y. R.; Kim, K. N.; Kim, Y. H., Yu, Q. J. *Appl. Phys. Lett.* **2017**, *110*, 203702.

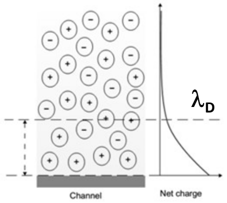
Mechanism 2 : Electron transfer



e.g. Redox reactions on the surface of graphene FET

Improvement : Increase the Debye length

Debye length [λ_D] = Thickness of the electric double layer



Maehashi, K.; Ohno, Y.; Matsumoto, K. *Nanobiosensors in Disease Diagnosis* **2016**, *5*, 1-13.

Biomolecules larger than λ_D cannot be detected.

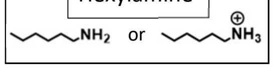
$$\lambda_D = 0.35\, I^{-1/2}$$

I : inonic strength

Weak ionic strength
⟶ Detection of large molecules

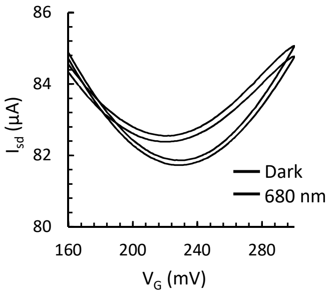
Introduce hexylamine to increase the Debye length

Hexylamine



Results – Light irradiation and CNP shifts

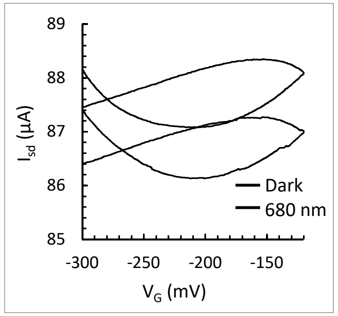
Without hexylamine



No shift in the CNPs

Positive CNP (+227 mV)

With hexylamine

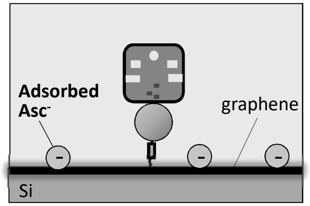


Unstable *I-V* curves

Negative CNP (-203 mV)

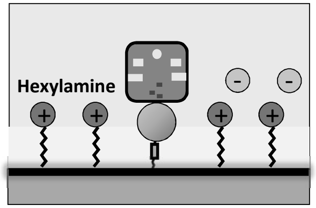
Effect of hexylamine

Without hexylamine



Adsorbed anions
→ Positive CNPs

With hexylamine



Adsorbed hexylamine
→ Negative CNPs

Hydrophobic environment was introduced by hexylamine.

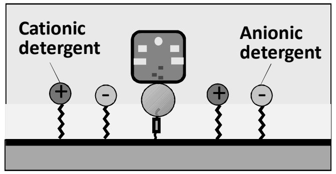
The *I-V* curves were unstable under the negative V_G.

Conclusions

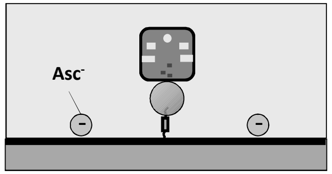
- Gold nanoparticles and photosystem I were immobilized on graphene field effect transistors to fabricate a light sensor.
- Light irradiation induced slightly positive shifts in the charge neutrality points of graphene.
- Further improvements would be possible by optimizing the electrolyte composition.

Two possible solutions

1. Use cationic and anionic detergents



2. Decrease the concentration of the electrolyte



Increase in the Debye length & Neutral surface charge

→ Improvement in the sensitivity toward the light