湿式法とALDの融合に基づく 酸化ニッケル膜の作製: 光学・電気化学デバイスへの展開

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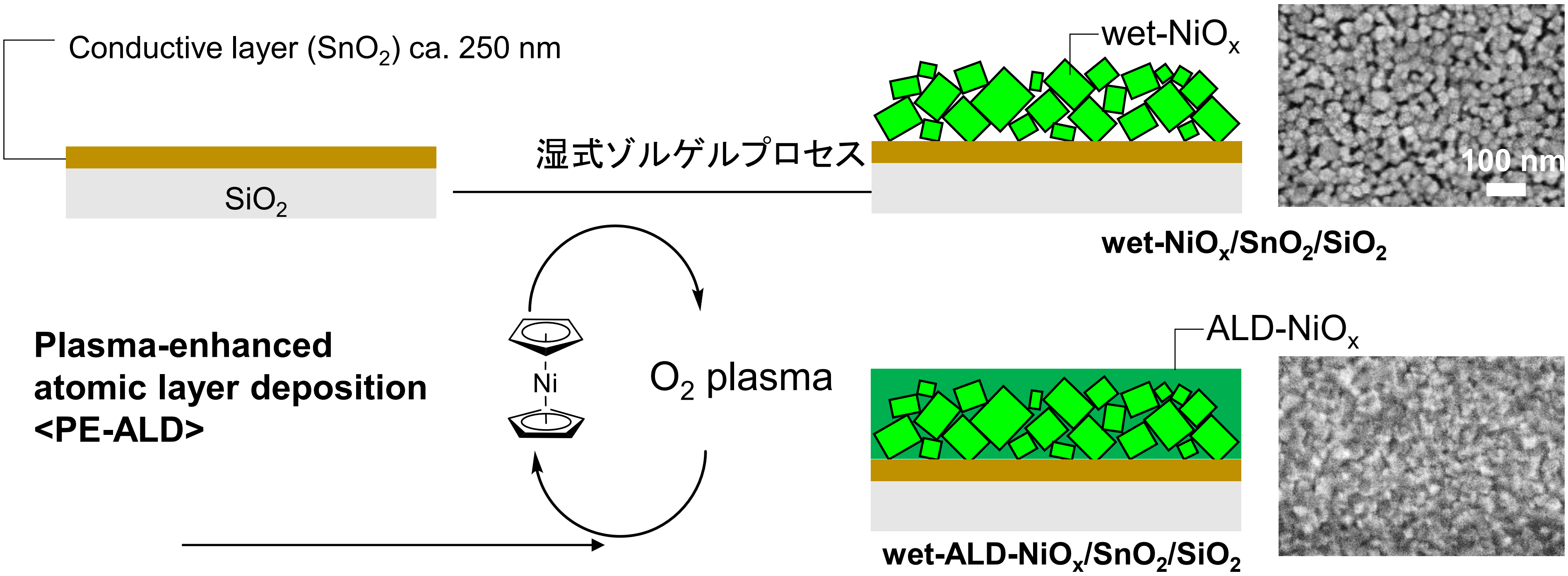
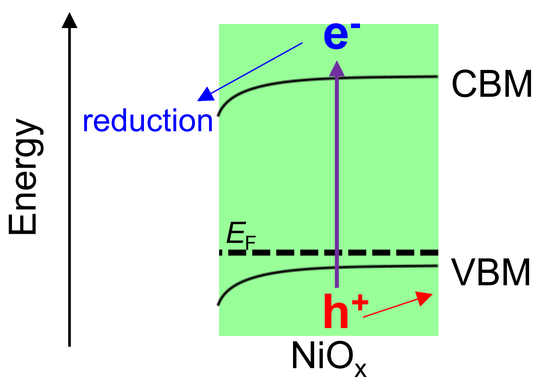
2025年度 第1回ARIM量子・電子マテリアル領域セミナー
施設共用におけるALD成膜のユーザー事例紹介
2025年8月6日
オンライン

概要：湿式法とALDの融合に基づく酸化ニッケル膜の作製



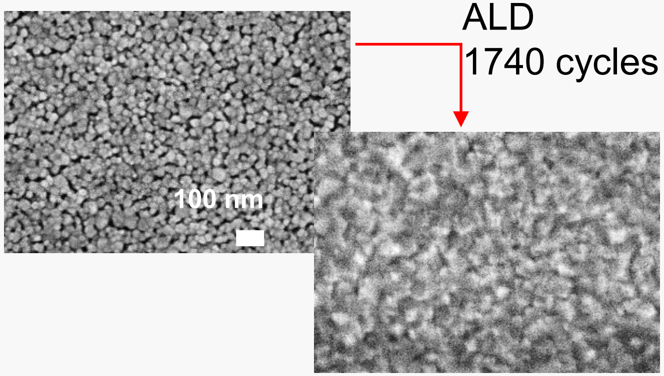


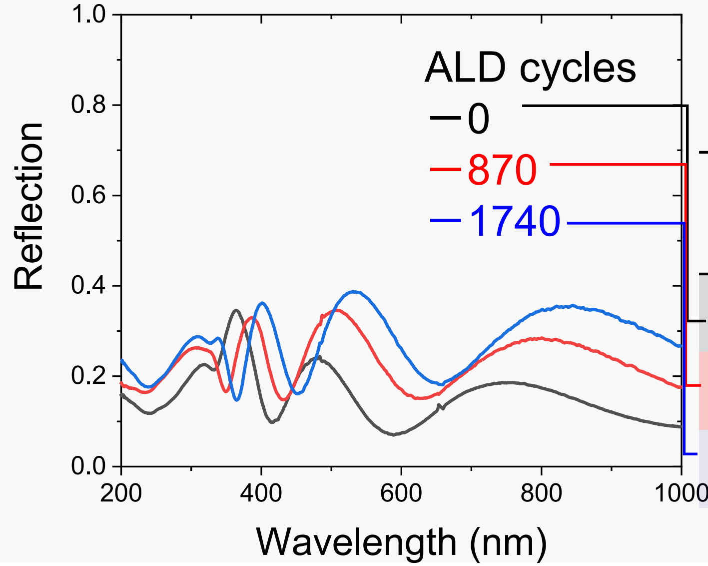
✓高効率光カソードのためのワイドバンドギャップp型半導体層

✓粒子内・粒子間のホール輸送能の向上を目指し、
湿式による高結晶性粒子＋気相プロセスで空隙充填

Morphologies and optical properties of NiO_x by wet+PE-ALD

Wet: 0.5 mol $Ni(OCOCH_3)_2$

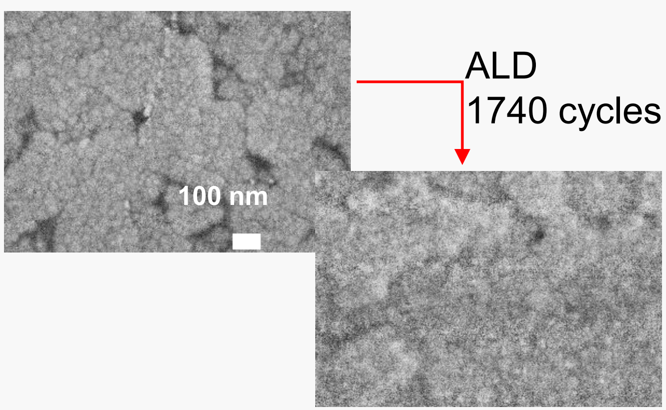


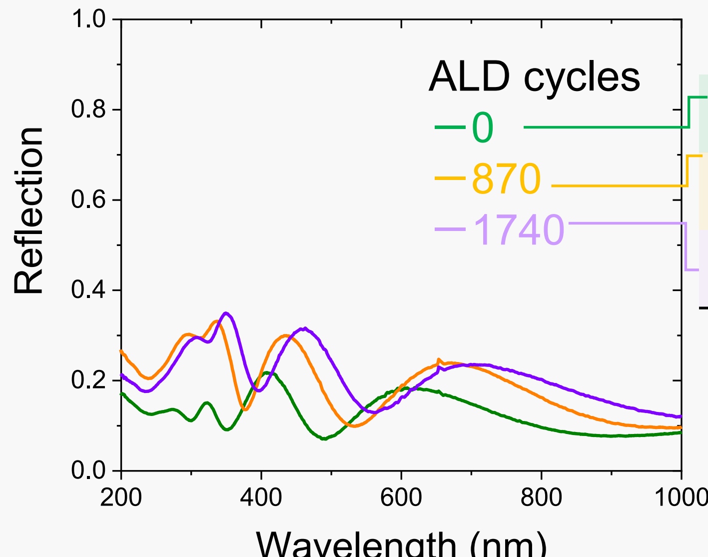


Thicknesses, refractive indices at 632.8 nm estimated by thin-film simulation

Thickness (nm)	*n*	*k*
not converged	1.97	0.05
47	2.41	0.11
68	2.43	0.01

Wet 1.0 mol $Ni(OCOCH_3)_2$





66	2.00	0.01
83	2.21	0.04
100	2.43	0.01

※deposition rate on flat surface: 15 nm per 870 cycles

✓ Volume of interparticle voids was reduced by ALD deposition.

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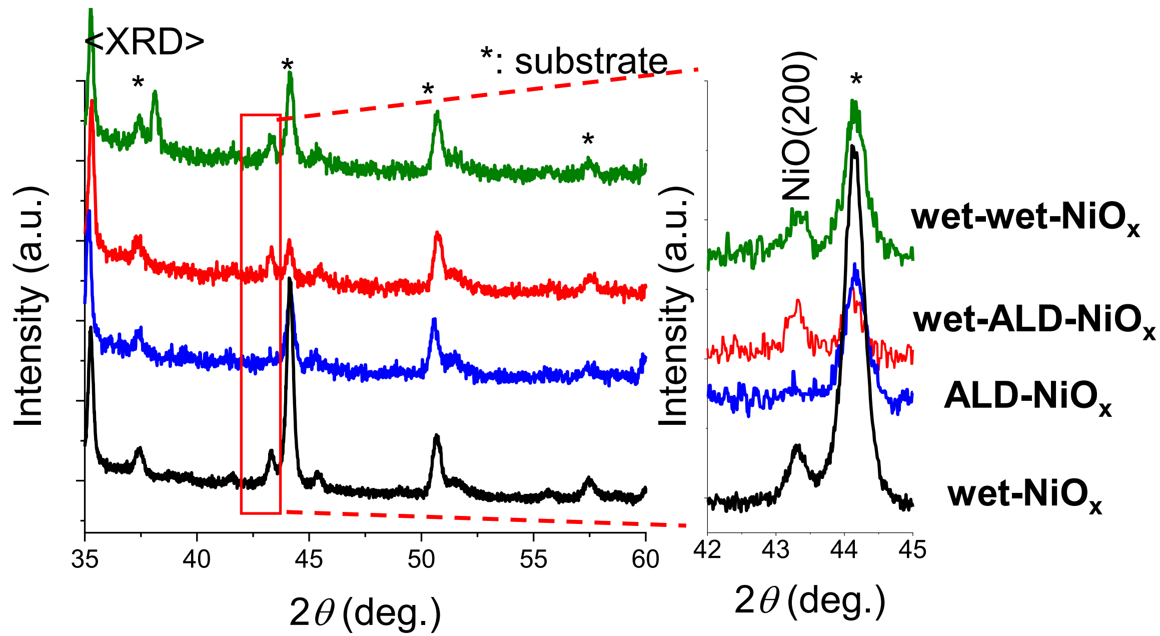
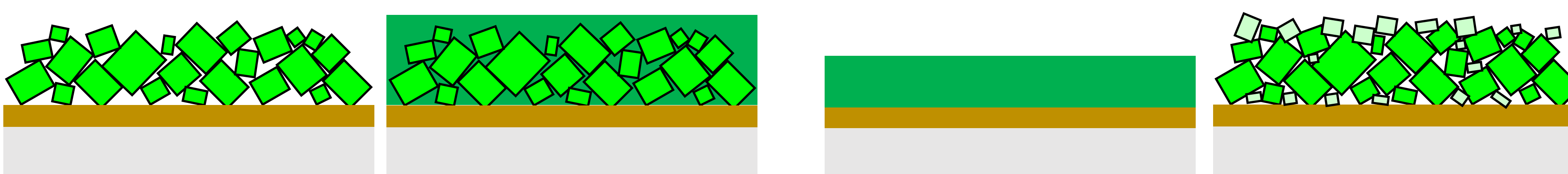
Comparison of structural properties among fabrication procedures of NiO_x



Density obtained by XRR

: 6.53 6.85 6.84 6.68



wet-NiO_x/SnO_2/SiO_2 wet-ALD-NiO_x/SnO_2/SiO_2 ALD-NiO_x/SnO_2/SiO_2 wet-wet-NiO_x/SnO_2/SiO_2

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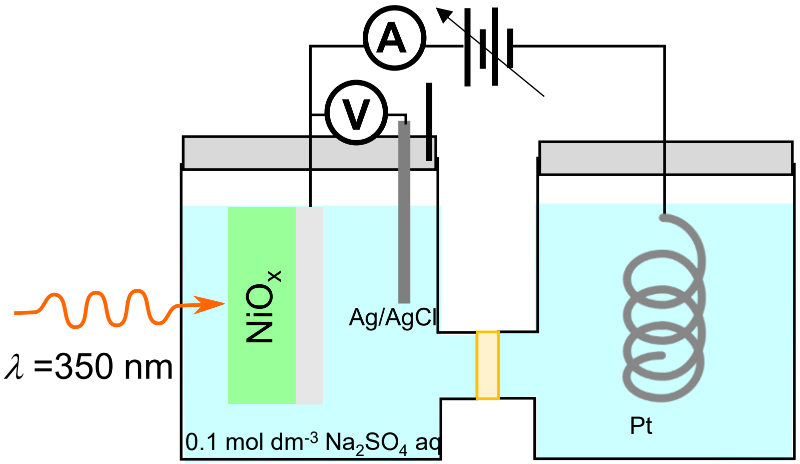
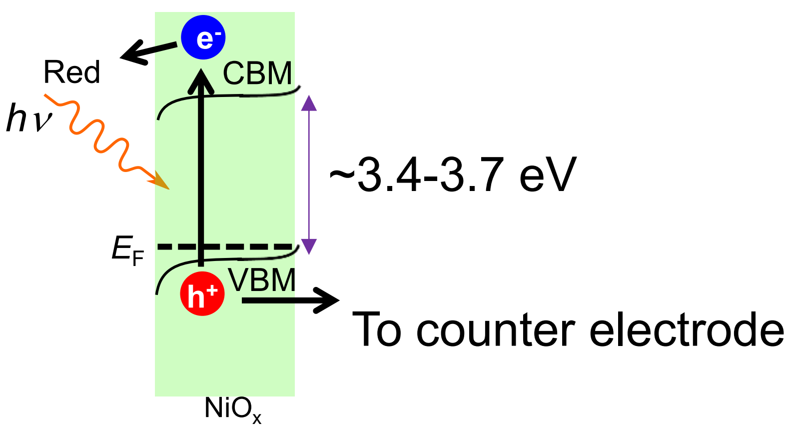
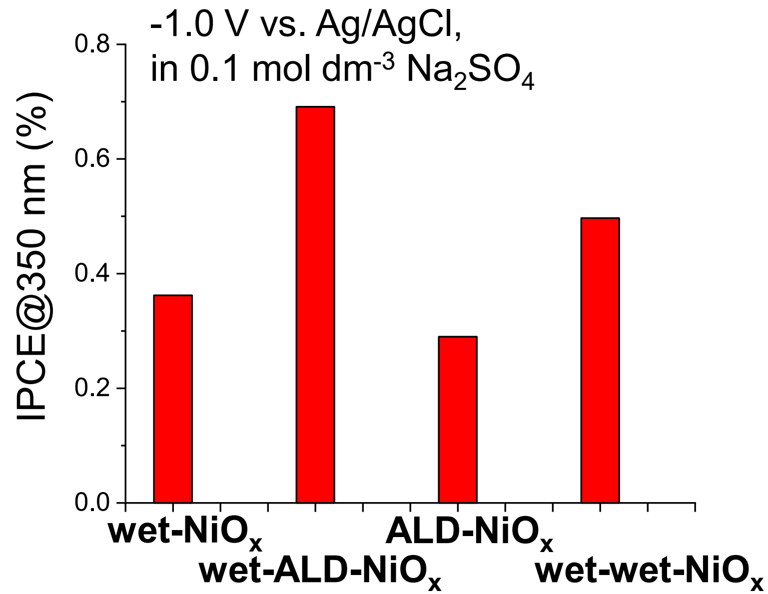
Photoelectrochemical properties of NiO_x







✓Charge separation efficiency of wet-ALD-NiO_x was larger than those of wet-NiO_x and ALD-NiO_x

✓Crystallinity and boundary void affect the photoelectrochemical properties of NiO_x cathode.

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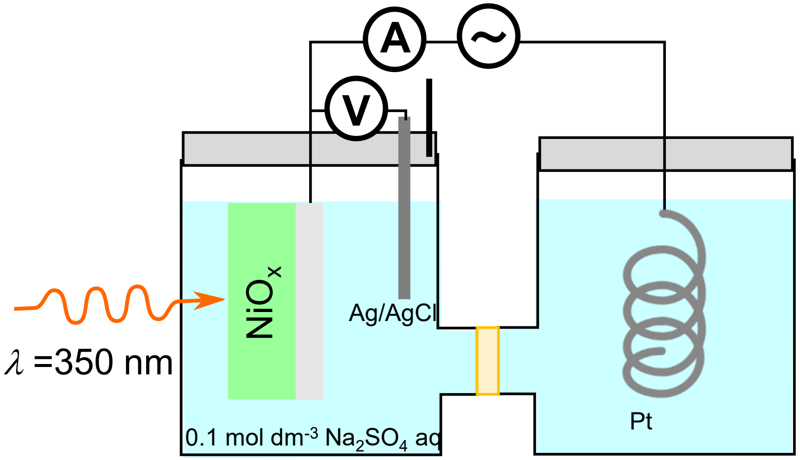
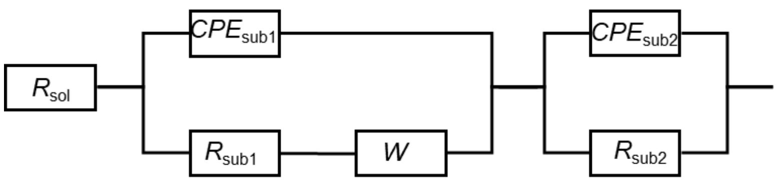
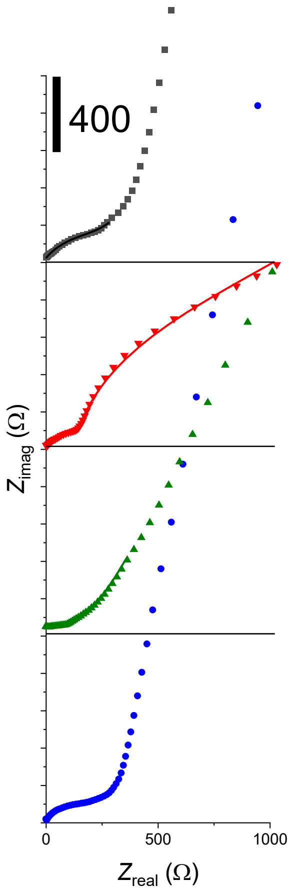
Electrochemical impedance spectra of NiO_x







Sample	R_{sub1} (Ω)	R_{sub2} (Ω)
wet-NiO_x	302	-
wet-ALD-NiO_x	157	838
wet-wet-NiO_x	229	209
ALD-NiO_x	11100	-

✓Two-step coatings contain the two impedance (NiO_x) components.
✓Secondary NiO_x support the hole migration between primary NiO_x particles.

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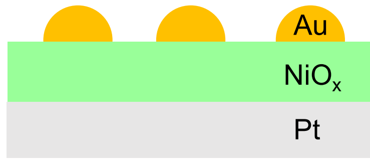
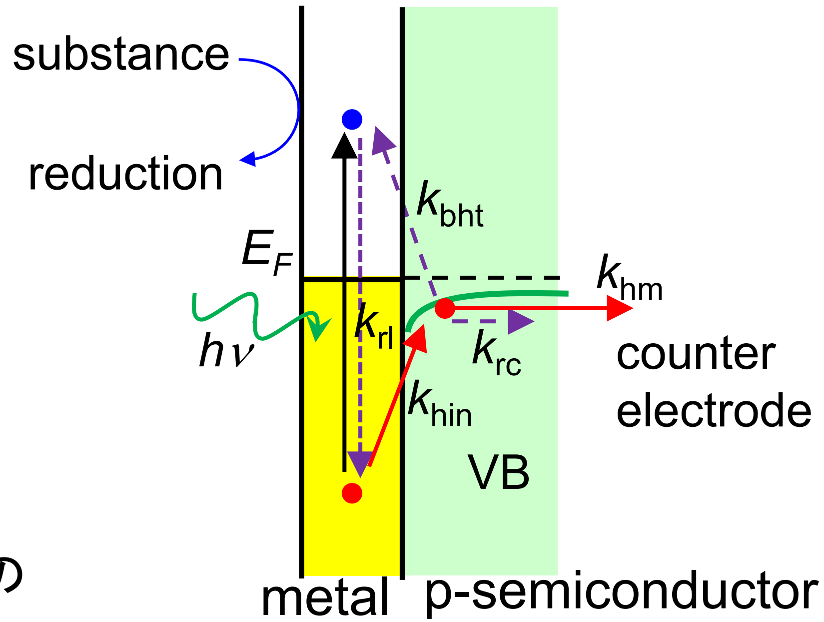
応用:プラズモン・平面共振器から成るモード結合光カソード



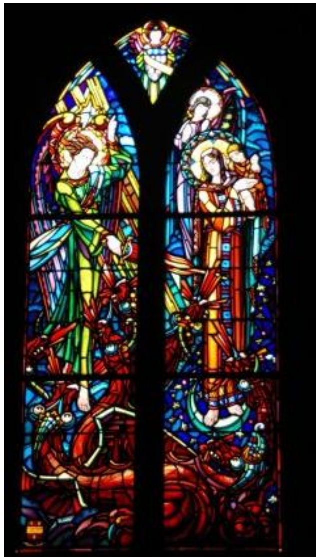


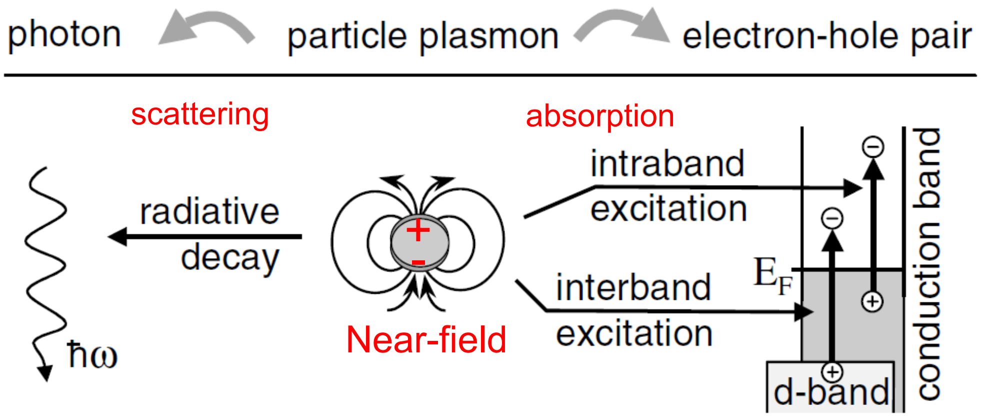
✓局在プラズモンと平面型共振器の光モード同士を結合
→高光吸収・ホール注入効率

✓共振器のp型半導体層としてNiO_xを利用
→膜物性による注入されたホールの輸送効率の向上

k_{rl}: electron-hole relaxation in Au
k_{hin}: hole injection
k_{bht} : back hole transfer
k_{rc}: electron-hole recombination in NiO
k_{hm}: hole migration

Localized surface plasmon resonance (LSPR)





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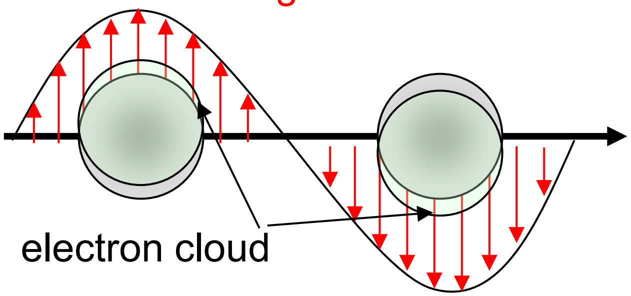

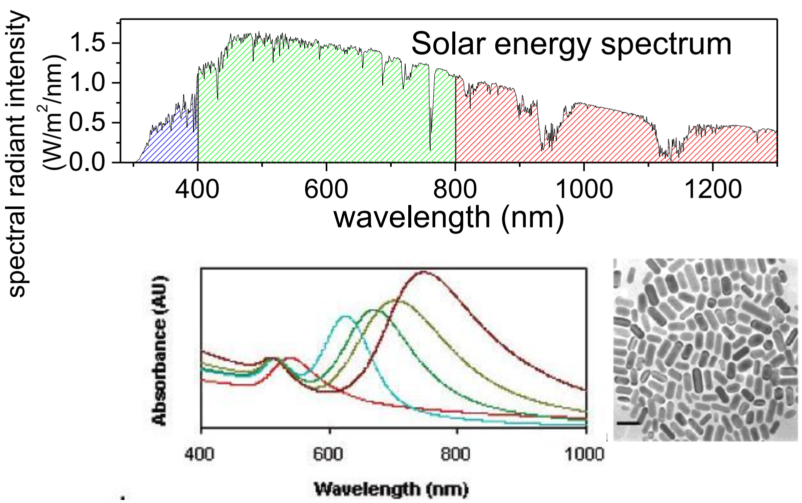

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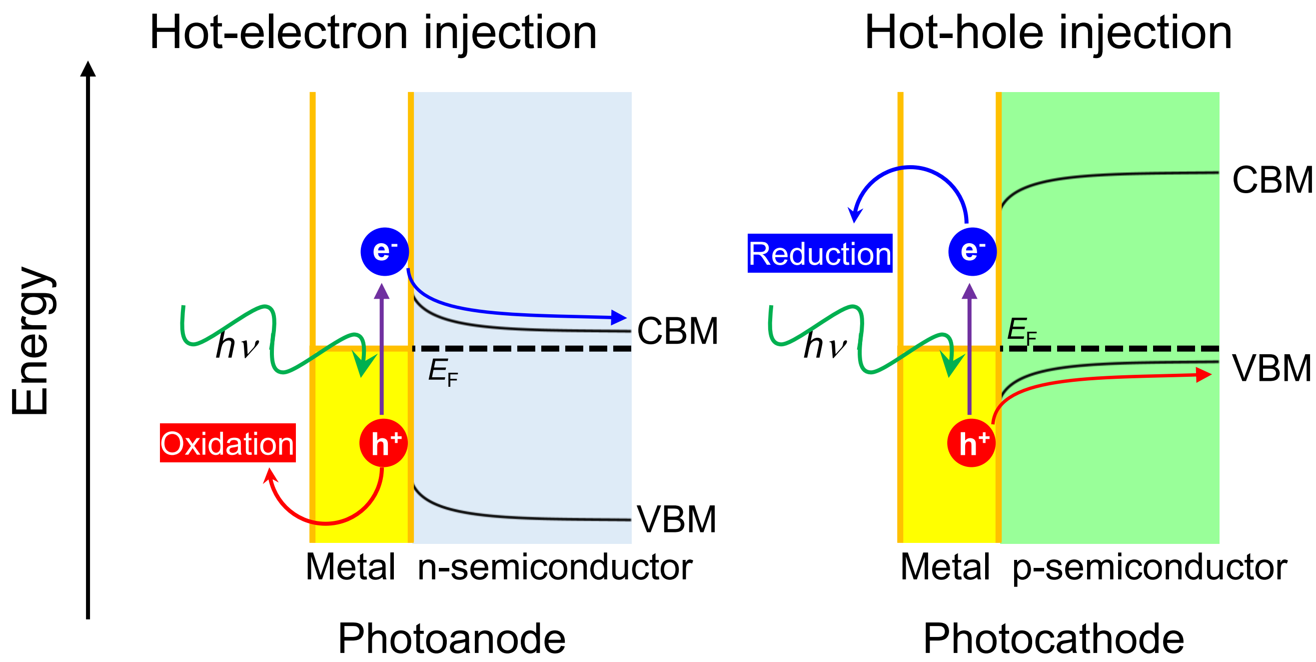
✓Spatial and temporal confinement of light
✓Arbitral control of resonant wavelength by size and shape of nanostructure

Plasmonic photoanode and photocathode



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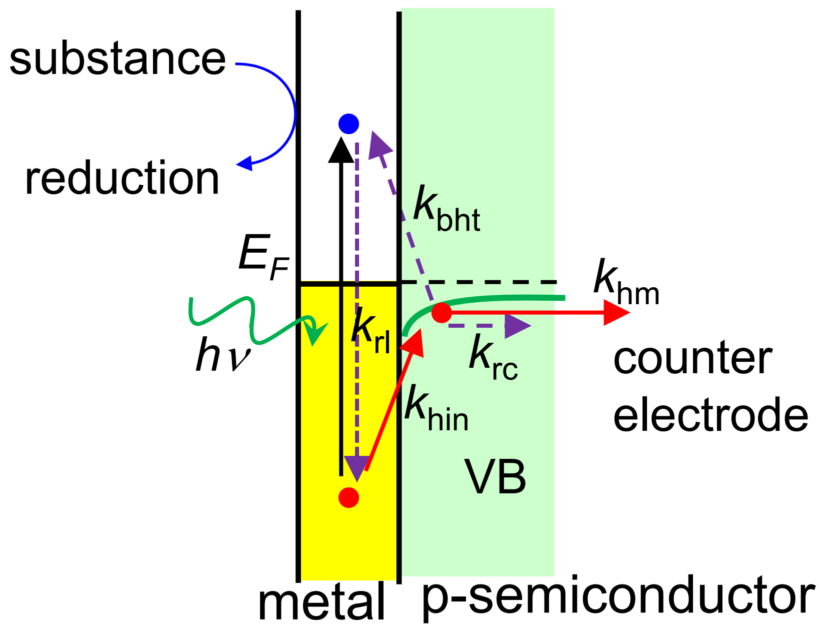
Y. Tajiri et al., *J. Phys. Chem. C* 2024, 128, 12339-12345.

CBM : Conduction band minimum
VBM : Valence band maximum
E_F : Fermi level

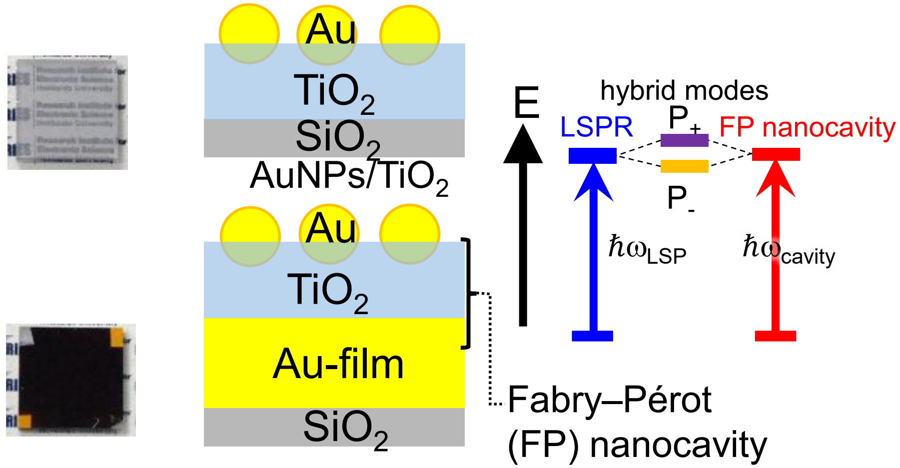
Essential hole transport pathways in plasmonic photocathode

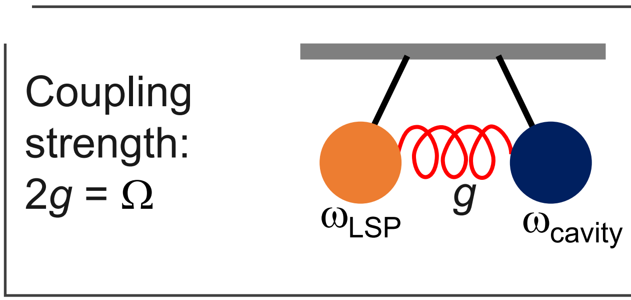


k_{rl}: electron-hole relaxation in Au
k_{hin}: hole injection
k_{bht} : back hole transfer
k_{rc}: electron-hole recombination in NiO
k_{hm}: hole migration

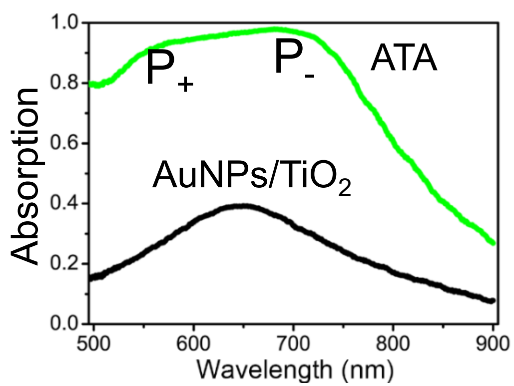
To improve the whole hole transport efficiency, we employ
✓Hole injection
→ Modal coupling (later mention)
✓Hole migration
→ Improvement of hole transport layer

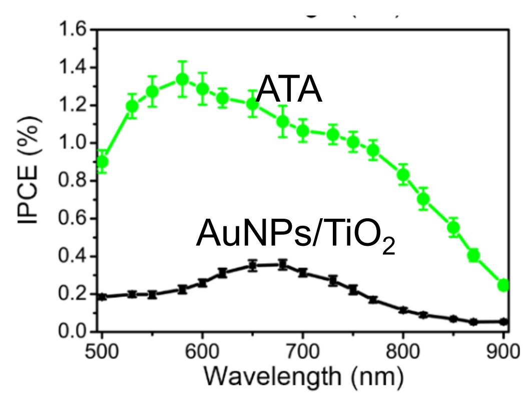
Modal strong coupling





$AuNPs/TiO_2$/Au film (ATA)→Strong coupling





※IPCE: incident photon -to-current efficiency (external quantum efficiency)

✓Absorption wavelengths were broadened.

✓Absorption efficiencies were >85% at 550-750 nm.

X. Shi, K. Ueno, T. Oshikiri, Q. Sun, K. Sasaki, H. Misawa, *Nat. Nanotechnol.* **2018**, *13*, 953-958.

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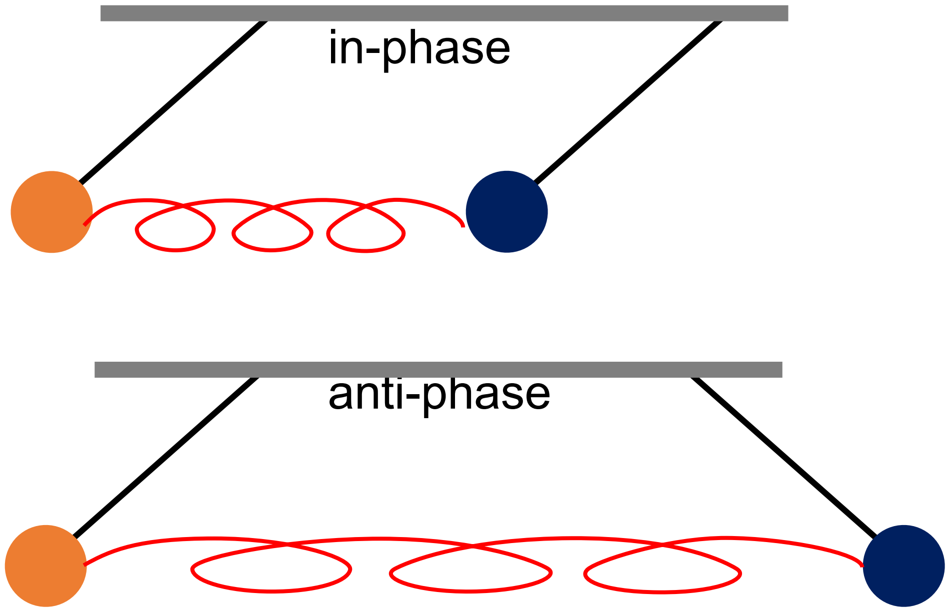
Modal strong coupling

<optical resonator>

<coupled harmonic oscillator : hybridized states>



$\hbar\Omega = 2g$

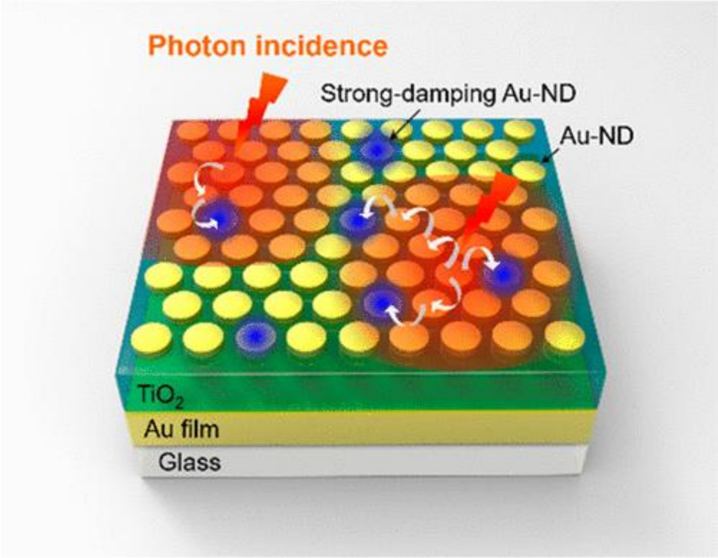
g: coupling strength

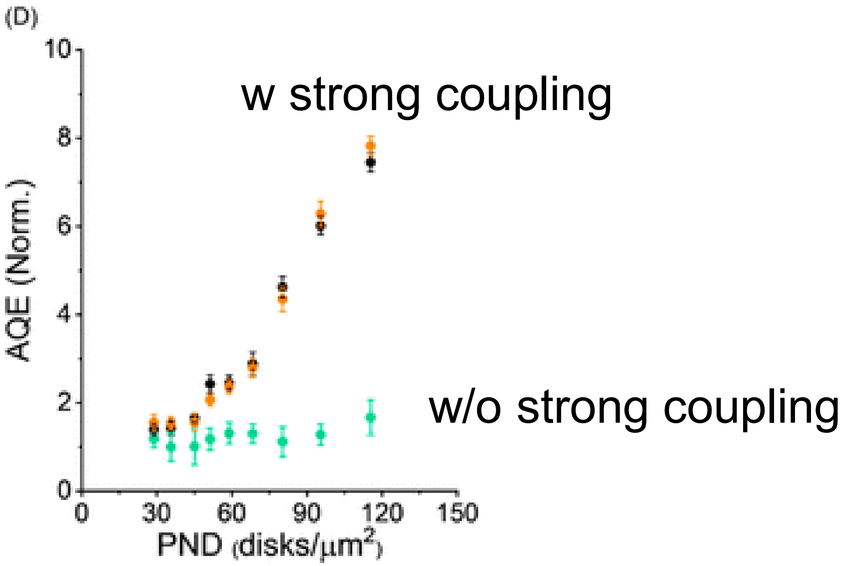
strong coupling condition:

$$\hbar\Omega > \sqrt{\frac{\gamma_{\mathrm{LSP}}^2}{2} + \frac{\gamma_{\mathrm{cavity}}^2}{2}}$$

γ_{LSP} , γ_{cavity}: full width at half maximum of LSPR and cavity

Quantum coherence under modal strong coupling can improve internal quantum efficiency





AQE = ΔODmax/*n*/*A*

n: the number of incident photons,

A: the absorption at the pump wavelength

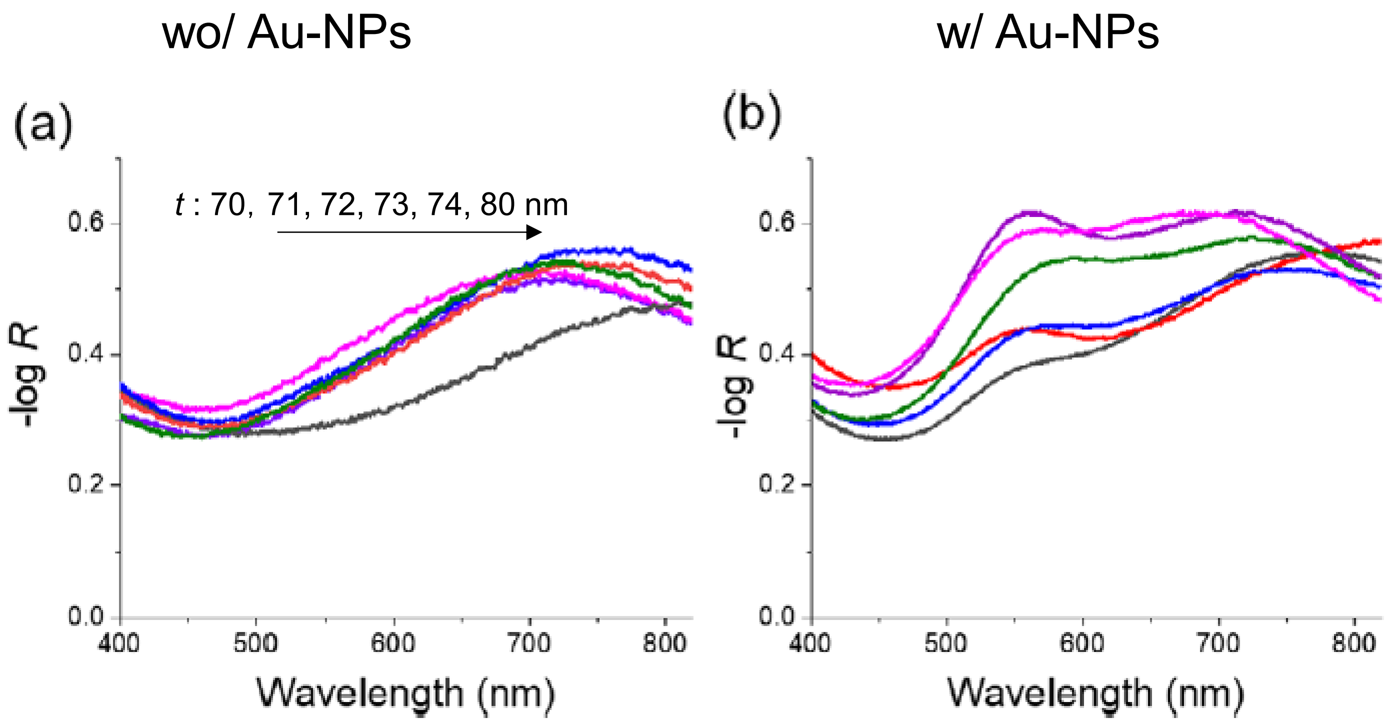
ΔOD_{max}: Amount of injected electron in TiO_2

✓Internal quantum efficiencies of the hot-electron injection increase as increase of particle number density (PND) of Au-ND.

✓Inside a coherence area, the more gateways would be available for the excited hot electrons to pass through and be injected into TiO_2.

Y.-E. Liu, X. Shi, T. Yokoyama, S. Inoue, Y. Sunaba, T. Oshikiri, Q. Sun, M. Tamura, H. Ishihara, K. Sasaki, H. Misawa, *ACS Nano* **2023**, *17*, 8315-8323.

Absorption spectra of Au-NPs/wet-wet-NiO_x/Pt



✓As the NiOx thickness increased, the resonance peak of the FP nanocavity exhibited a red shift.
✓After Au-NP loading, the absorption intensity increased, and the spectral bandwidth broadened.

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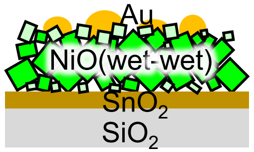
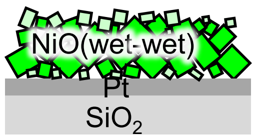
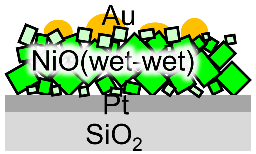
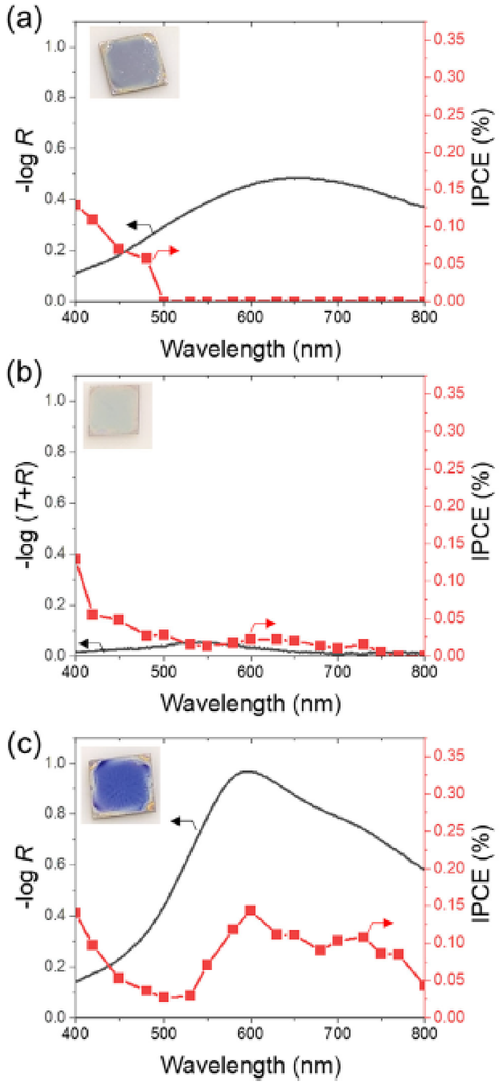
Photoelectrochemical reaction using photocathode under modal strong coupling condition

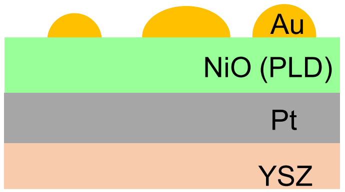




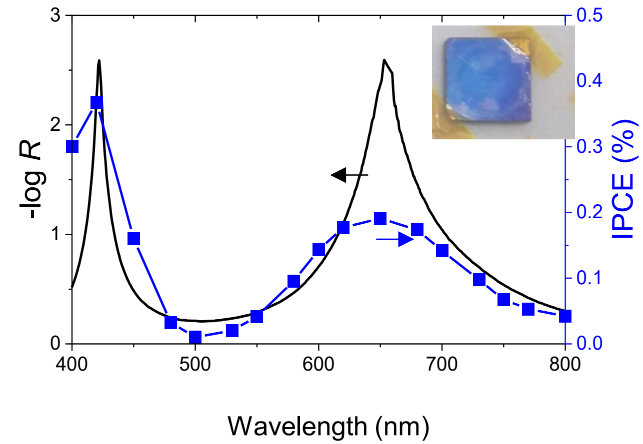




In 0.1 mol dm^{-3} Na_2SO_4 aqueous solution
-0.6 V vs Ag/AgCl



Au-NPs/NiO(PLD)/Pt film



In 0.1 mol dm^{-3} $KClO_4$ aqueous solution
-0.2 V vs Ag/AgCl

✓ Strong coupling dramatically enhanced photoelectrochemical performance based on hot-hole injection and reduction on the photocathode.

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Conclusion

✓ 湿式法とPE-ALDを組み合わせたNiO_x層の成膜法を開発し、高い結晶性を有するNiO_x粒子間の空隙を、ALD方により充填する方法論を見出した。

✓ 上記NiO_x層は高いホール輸送能を示し、光カソードの候補として有用であることがわかった。

✓ 上記方法論と同様の機序で、湿式多段階成膜を用いたNiO_x層を、プラズモン-光共振器結合形に適用することで、可視光に応答可能な光カソードの作製に成功した。

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