



WMIRF 2018 Early Career Scientist Summit



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Hot carrier engineering with titanium nitride nanostructures

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Marco Polo

“Zipangu (Japan) as a golden country”
(The Travels of Marco Polo, 13th century)



Kyoto, Japan

Gold nanostructures



gold (Au)

nanoscale



Au nanoparticle

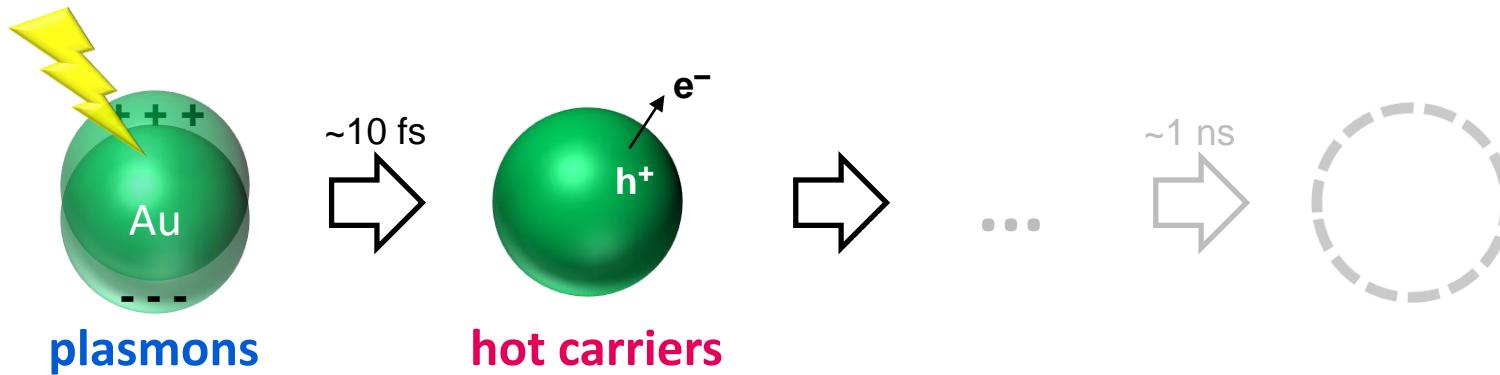
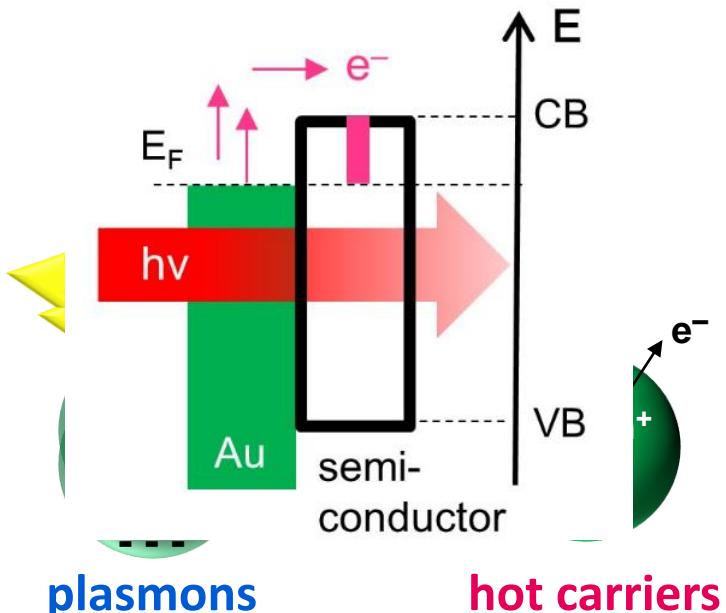
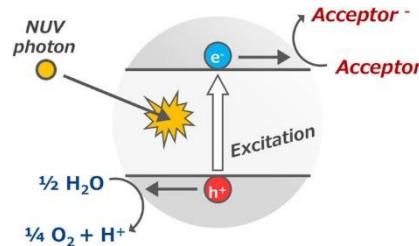


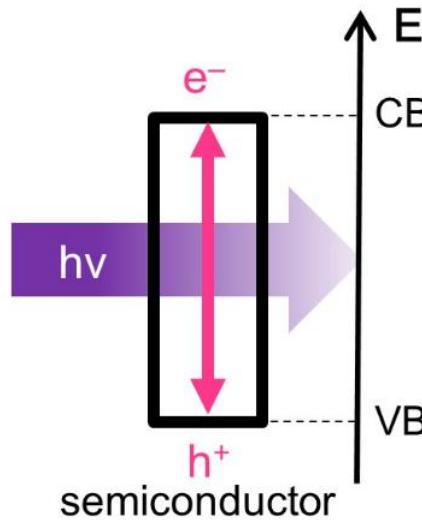
Photo-carrier excitation

Narita, et al, Sci. Rep. (2015);
© SHARP

Semiconductors

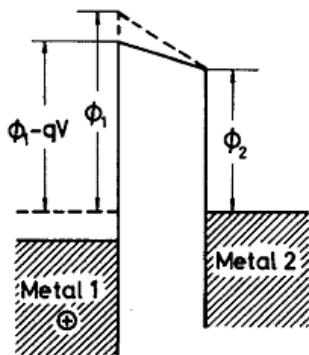
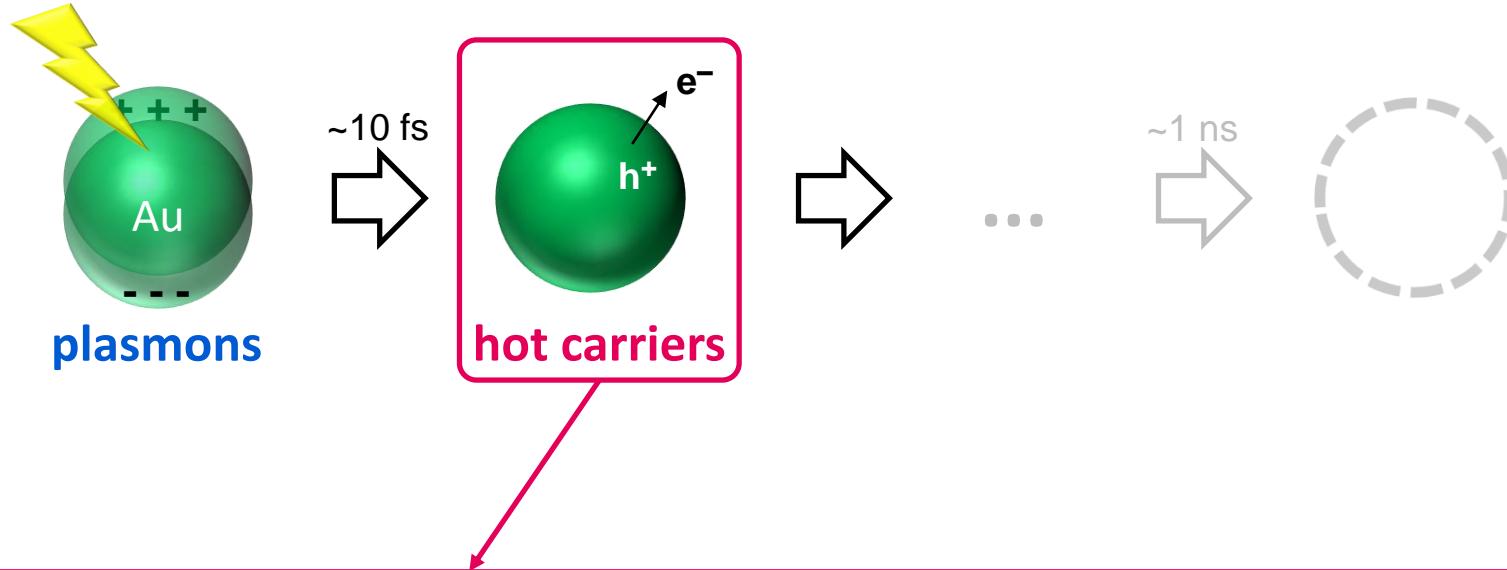


Sub-bandgap photo-excitation

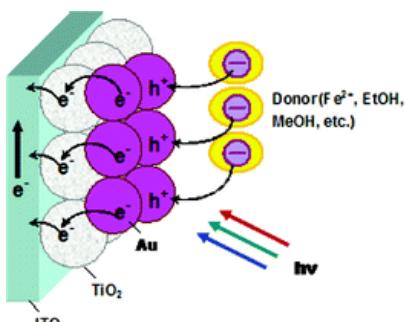


Bandgap limited photo-excitation

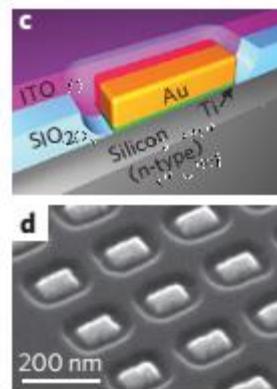
Hot carrier engineering



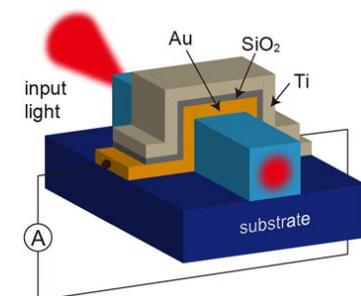
Visible photocurrent
K.H. Gundlach, et al, JAP
(1975)



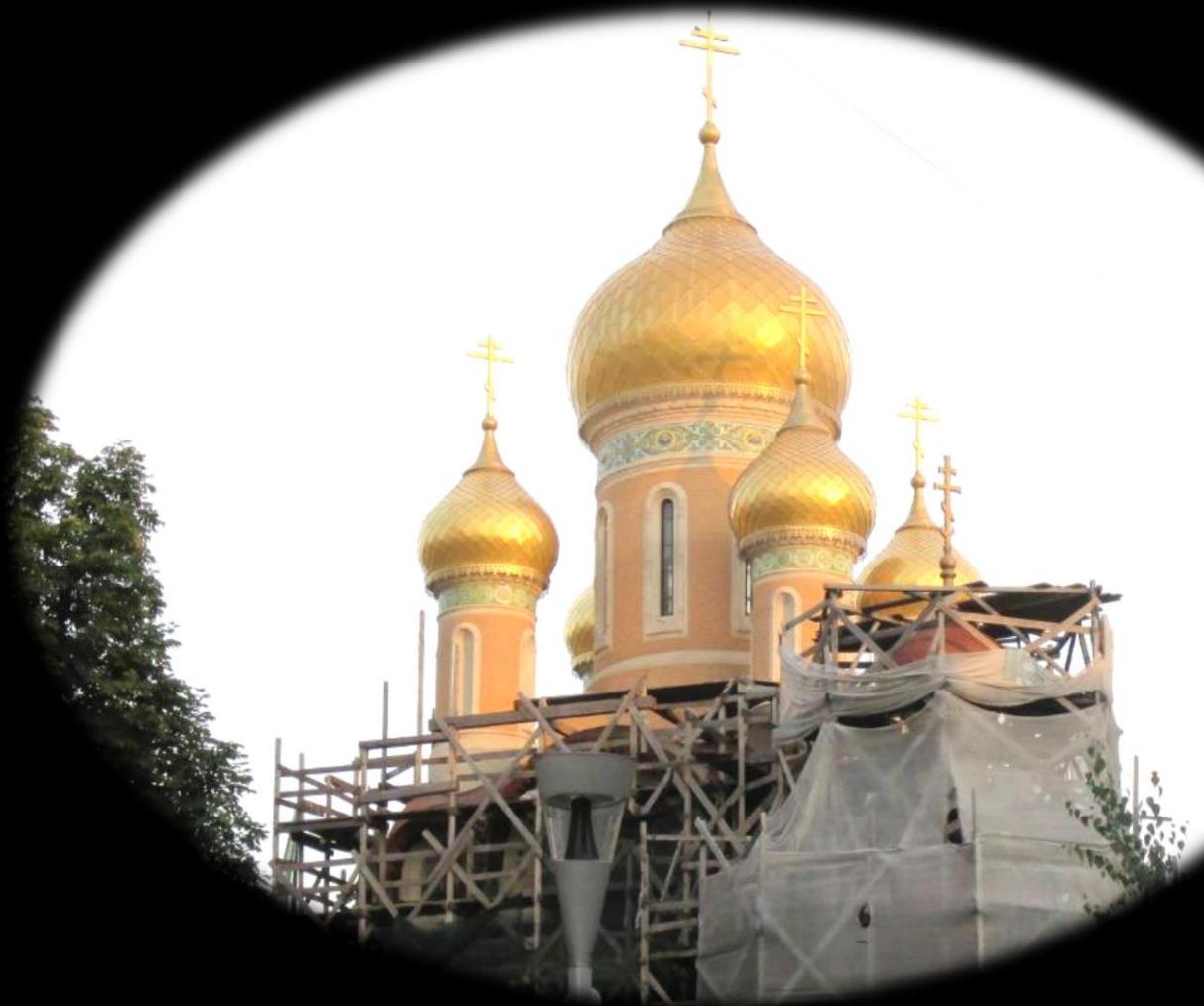
Visible photocatalysis
Tian & Tatsuma, Chem. Comun. (2004); Tian & Tatsuma, JACS (2005)



NIR Si detector
M.W. Knight et al, Science (2011)



Waveguide photodetector
S. Ishii, et al, ACS Photonics (2014)



Bucharest, Romania

Titanium nitride (TiN)

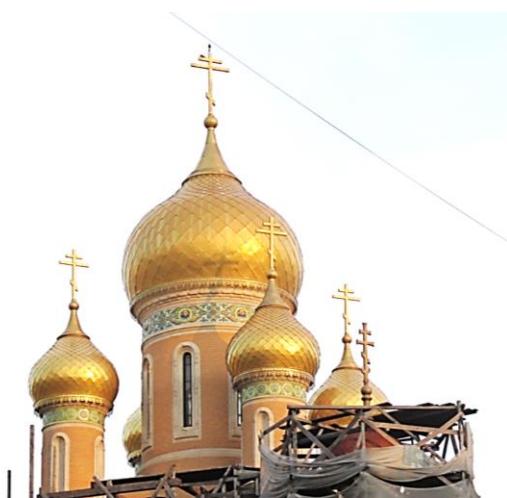


gold (Au)

nanoscale



Au nanoparticles



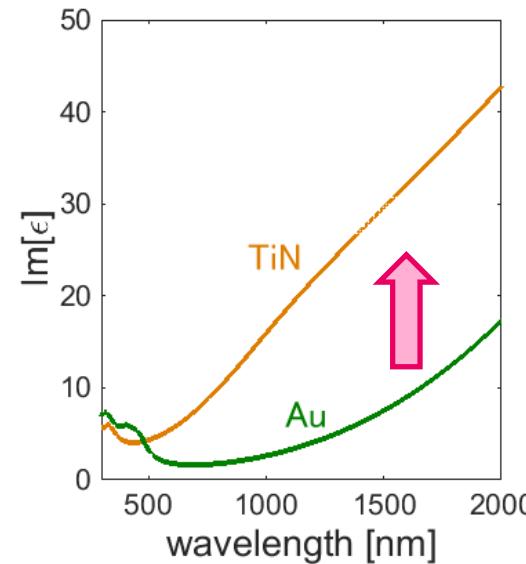
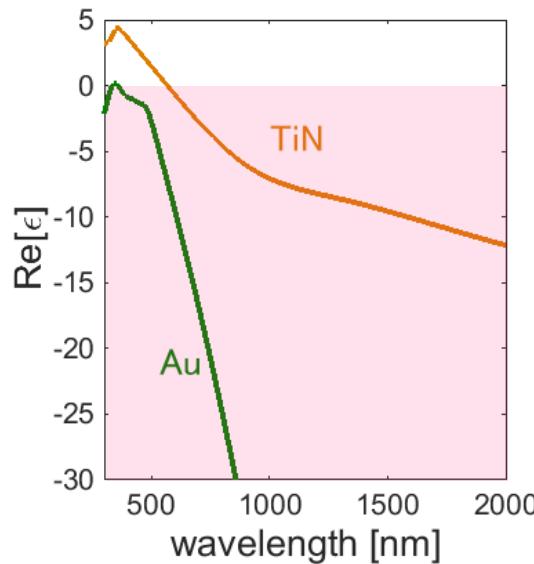
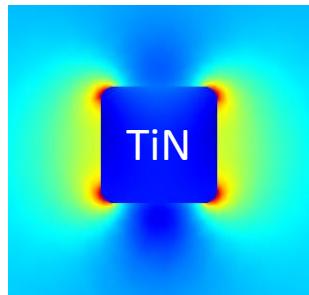
titanium nitride (TiN)

nanoscale

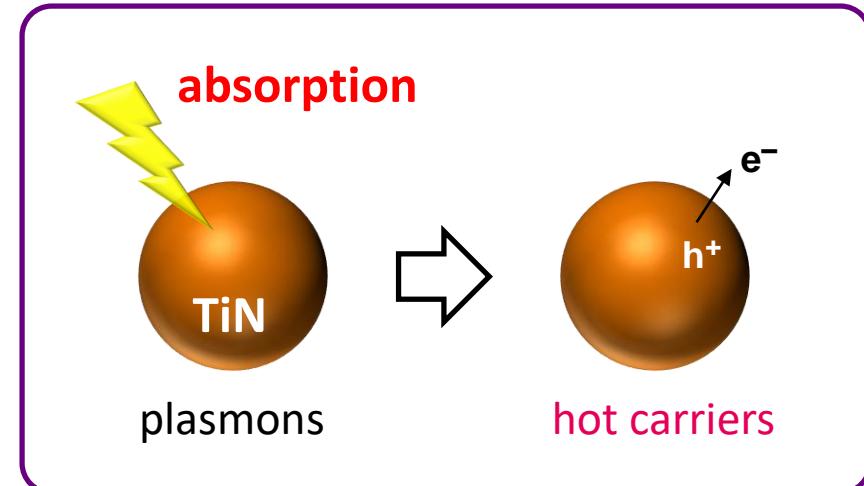


TiN nanoparticles

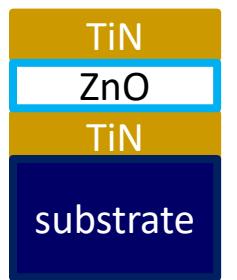
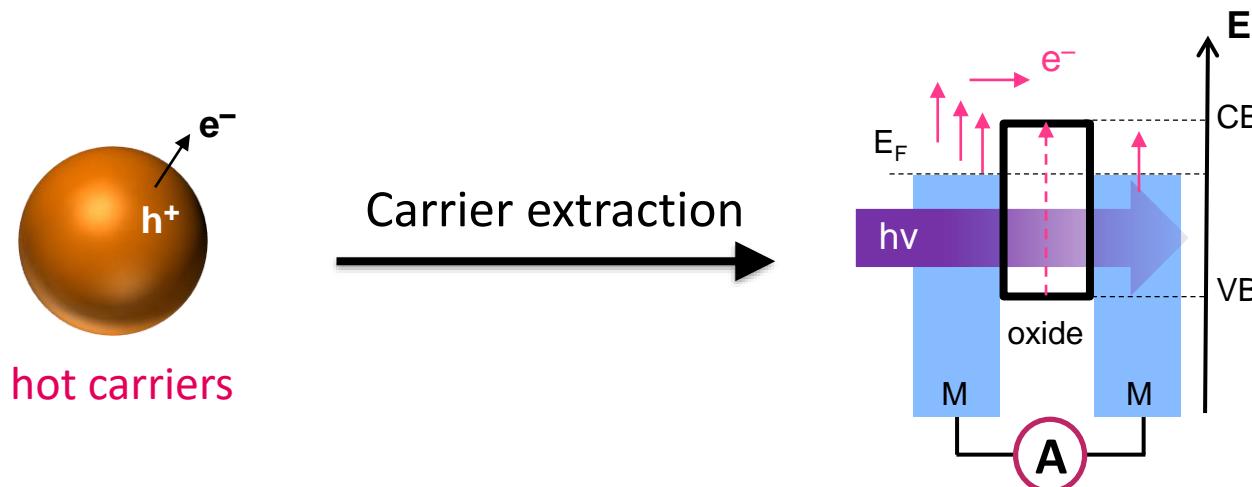
Dielectric function of TiN



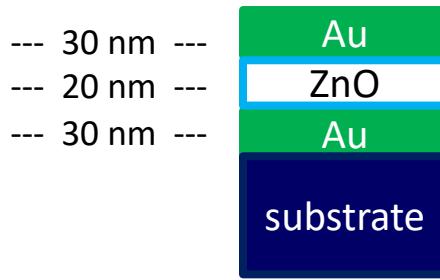
- $\text{Re}[\epsilon] < 0$
⇒ Plasmonic
- Large $\text{Im}[\epsilon]$
⇒ Strong absorption



Hot carrier excitation from nitride/metal

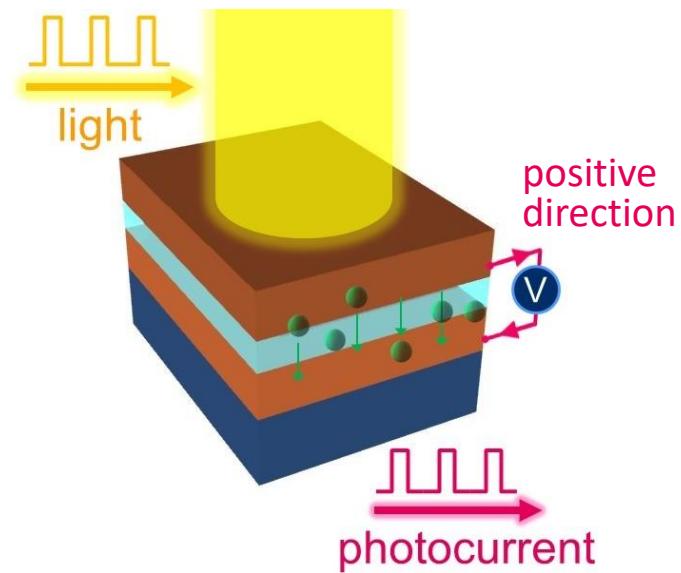


TiN/ZnO/TiN

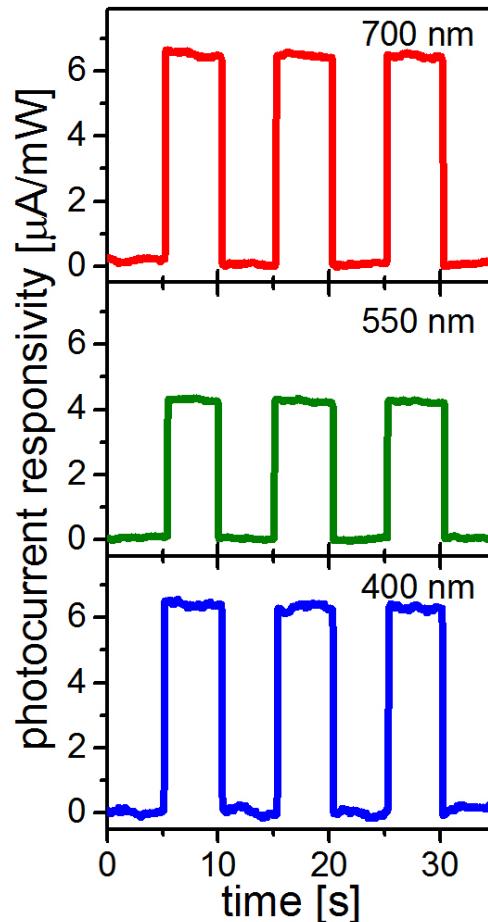


Au/ZnO/Au

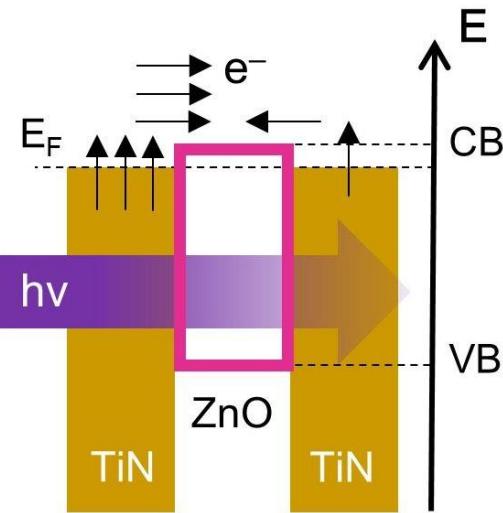
1. Thin film deposition by sputtering
2. Photocurrent measurement with a wavelength tunable light source (no bias voltage)



Photocurrent from TiN



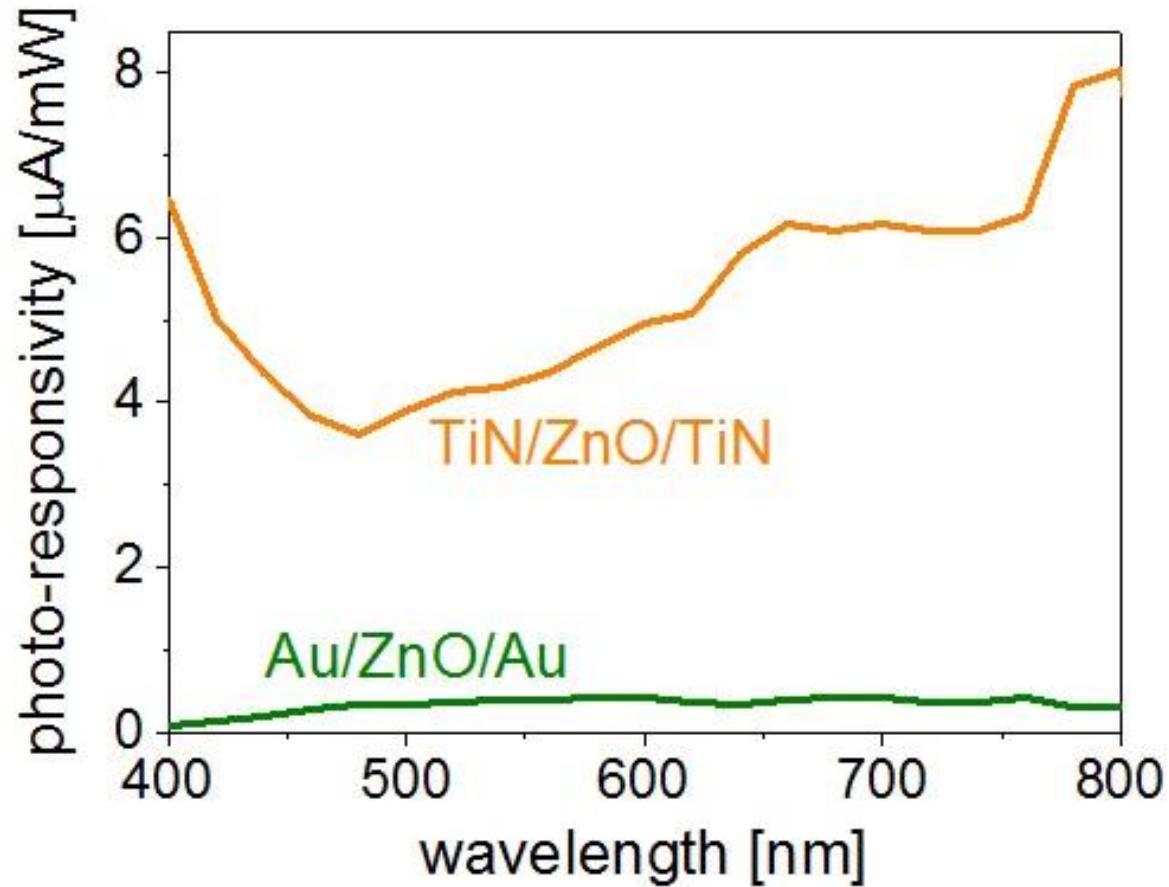
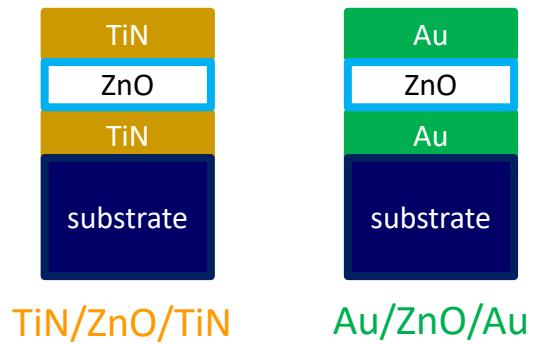
Visible photocurrent w/ TiN



- Bandgap of ZnO :
3.2 eV (388 nm)
- Hot electron excitation from TiN

S. Ishii, et al, ACS Photonics, 3, 1552 (2016)

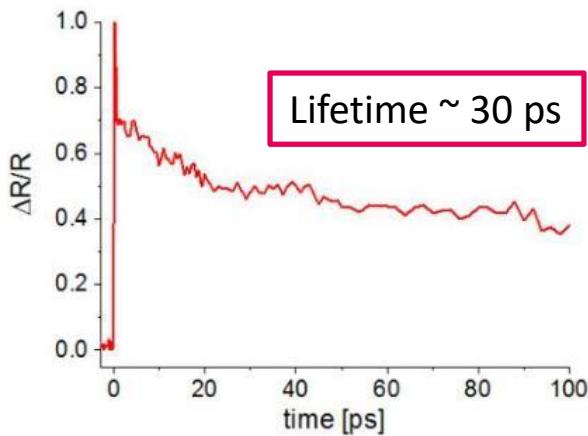
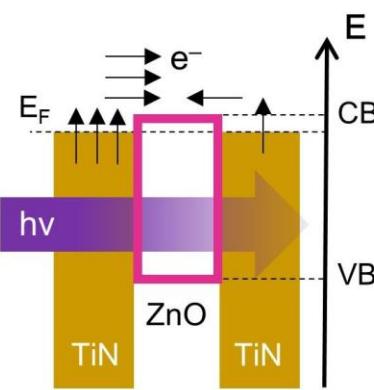
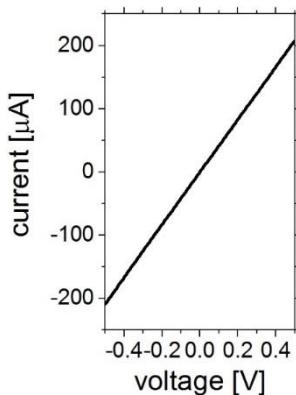
Comparison of TiN & gold



TiN can generate larger photocurrent than gold (Au)

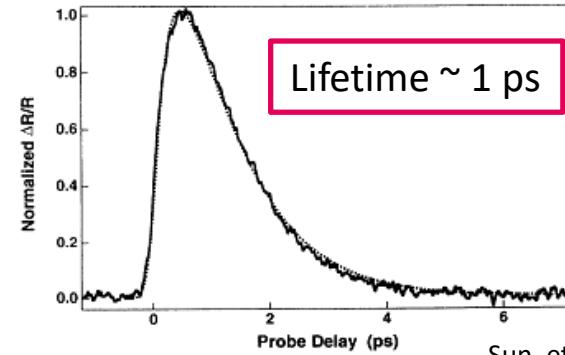
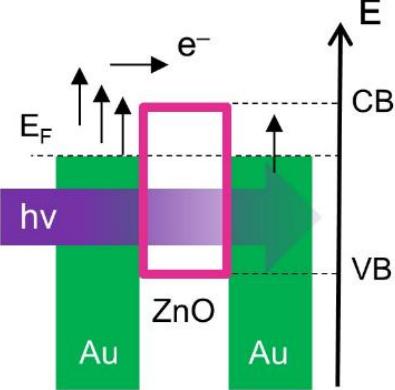
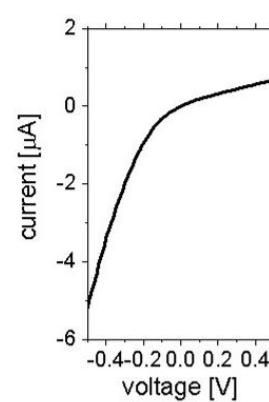
Electric properties

TiN



Lifetime ~ 30 ps

Au



Lifetime ~ 1 ps

Sun, et al, PRB (1994)

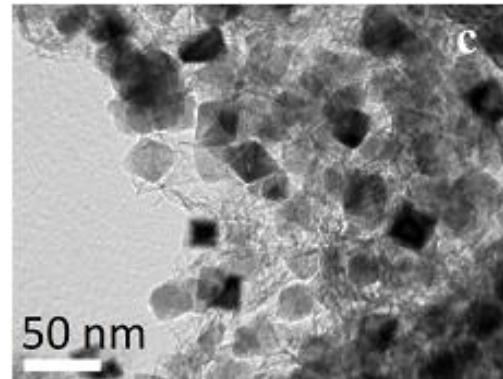
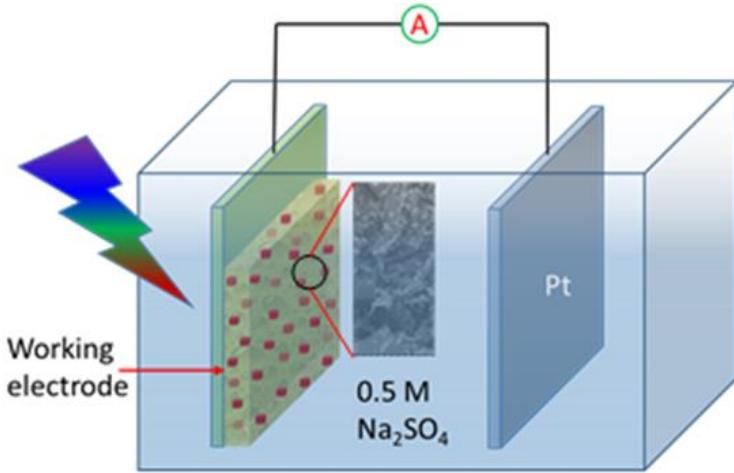


Y. Wada

- Smaller energy barrier for TiN
- Longer life time for TiN

TiN for visible photocatalytic activity

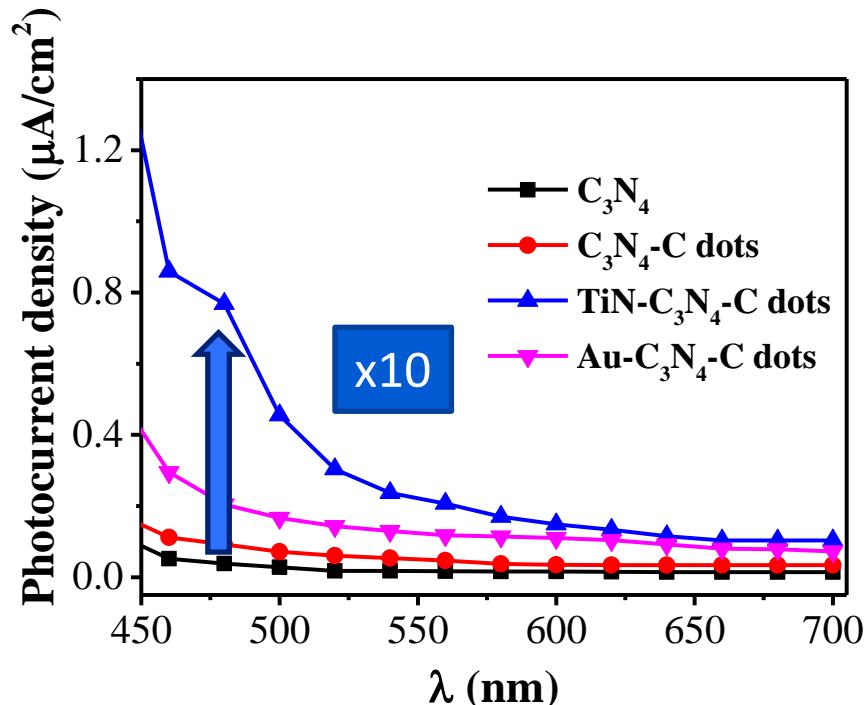
- Photocatalyst: C_3N_4
 - Metal-free, abundant
 - Bandgap: $\sim 2.7 \text{ eV}$
- Mixing TiN NPs to C_3N_4 for visible activity



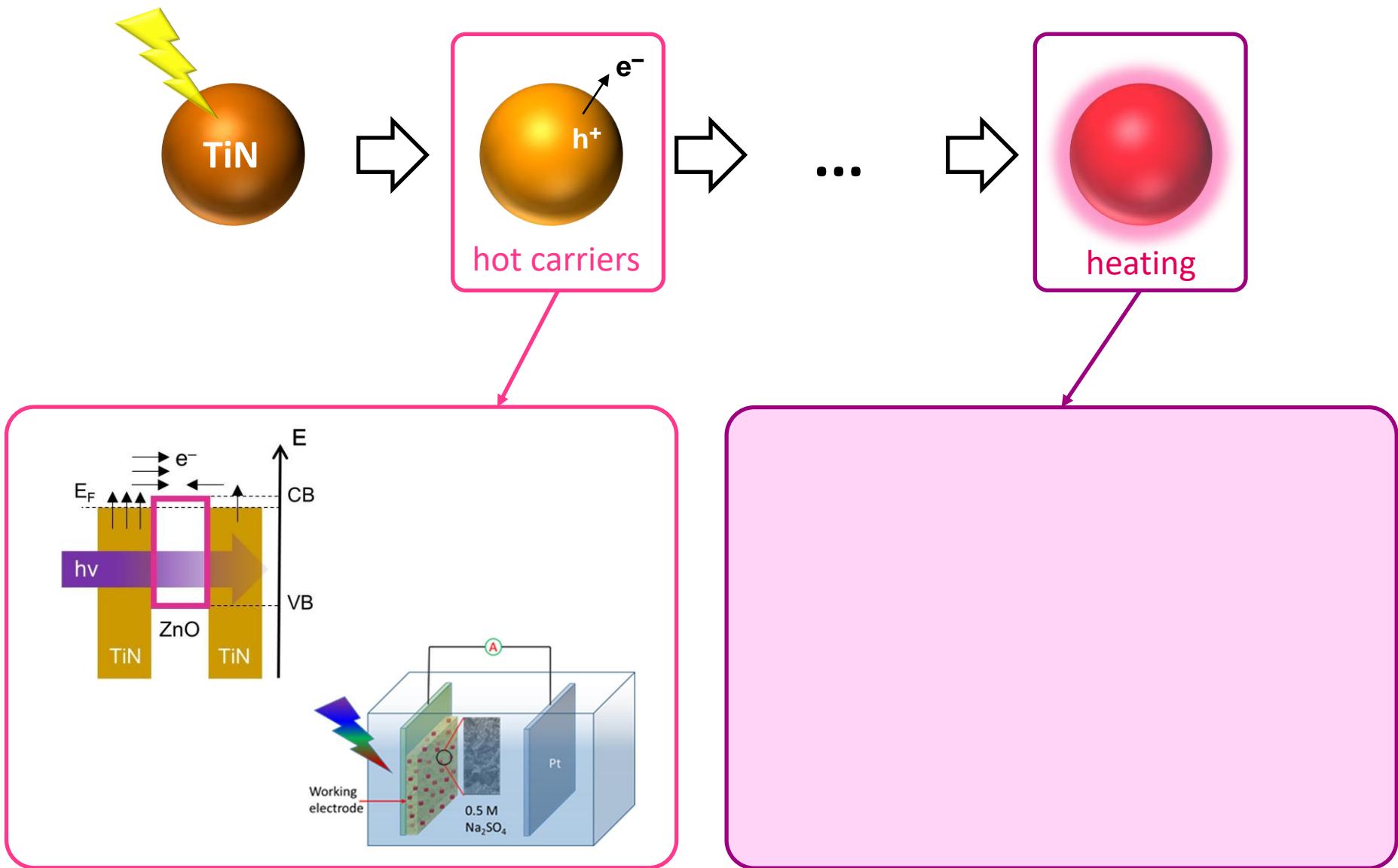
TiN NPs embedded C_3N_4 -C dots



S. Shinde

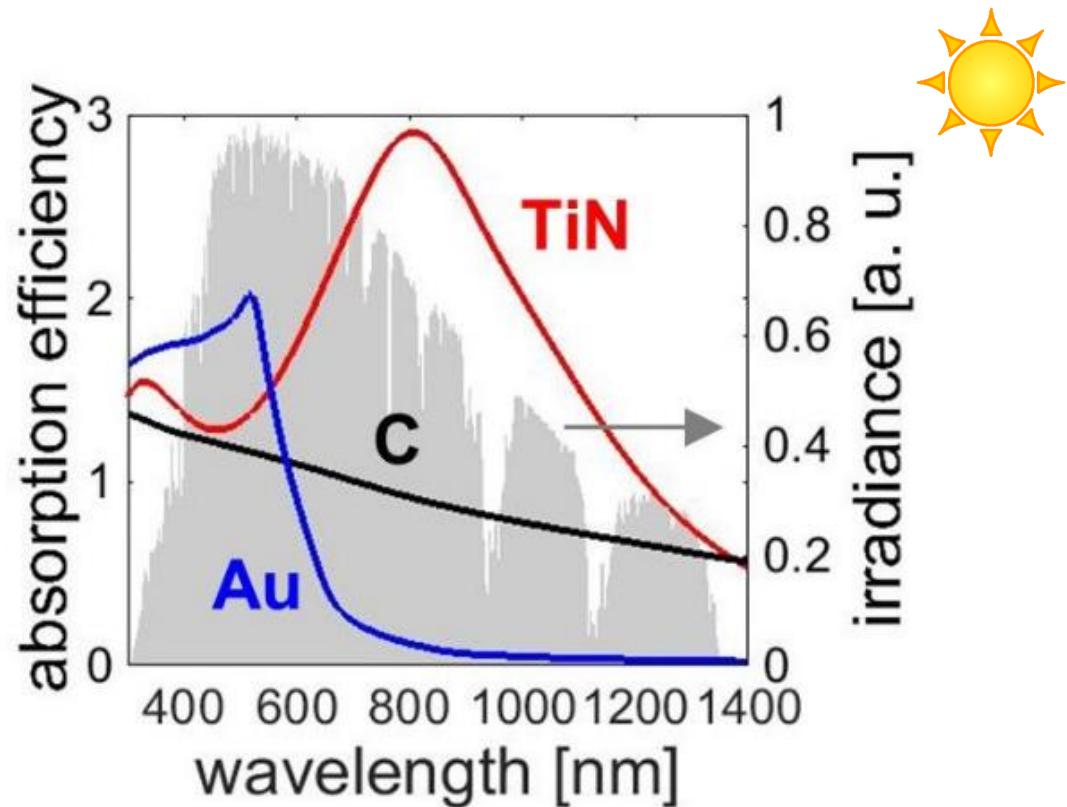
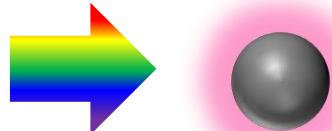


Photothermal heating with TiN



Sunlight absorption efficiency

Sunlight (AM 1.5)

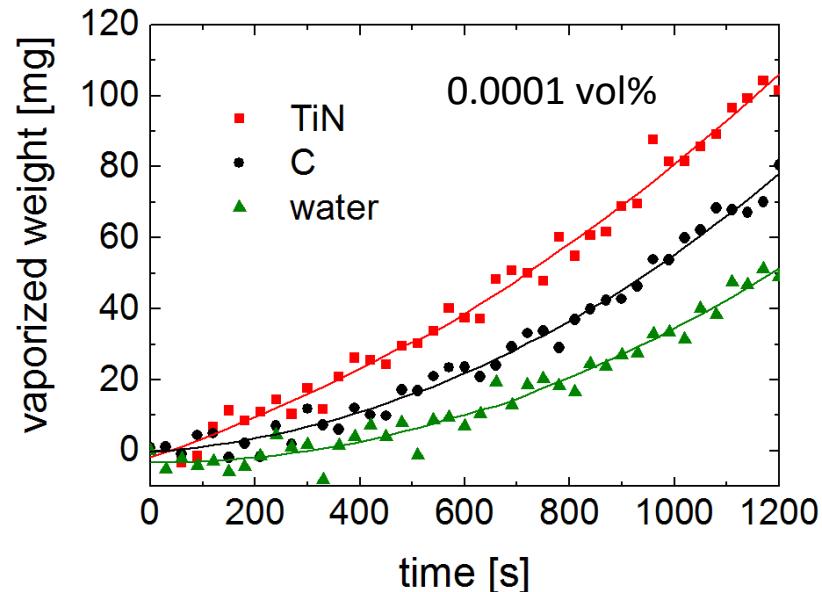
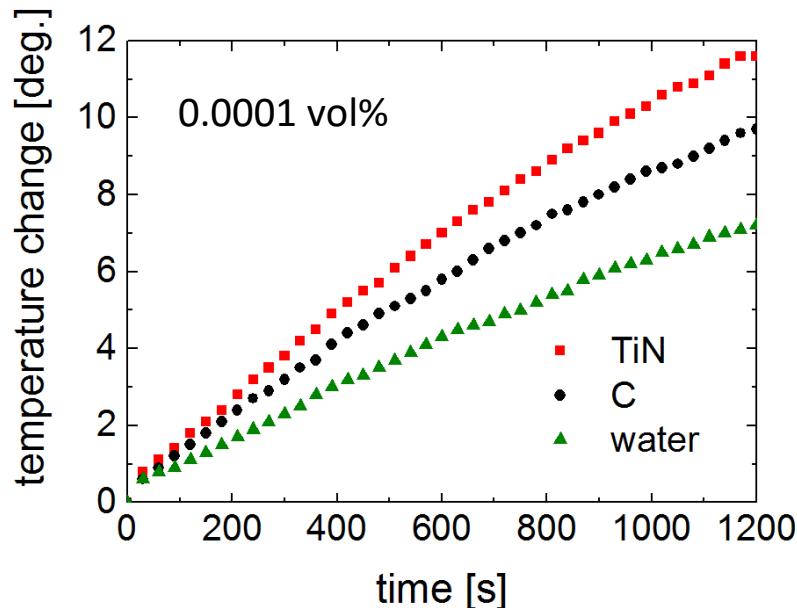
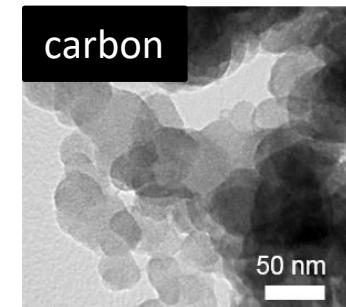
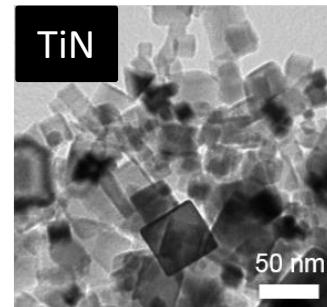


TiN NP absorbs more sunlight than Au NP and carbon NP

Solar water heating

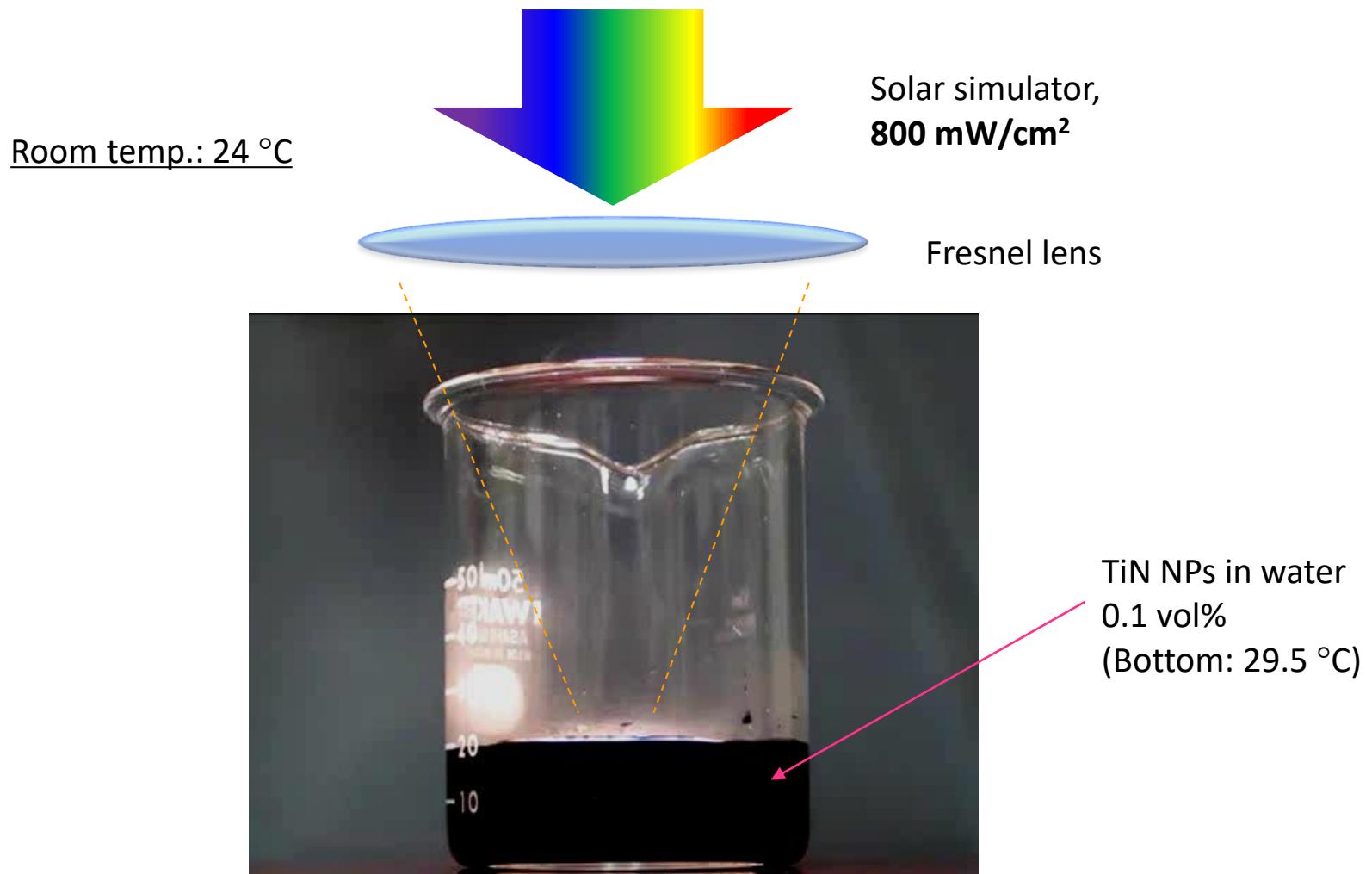
Solar simulator,
80 mW/cm²

Room temp.: ~20 deg. C



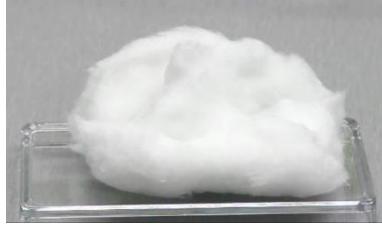
- TiN NPs have higher heating rates than carbon NPs
- Efficiency **~90 %** (0.1 vol%) <= solar cell: < 20 %

Solar vapor generation



S. Ishii, et al, J. Phys. Chem. C 120, 2343 (2016)

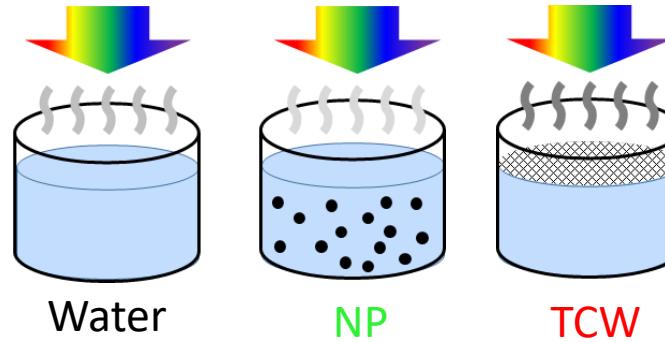
Solar water evaporation



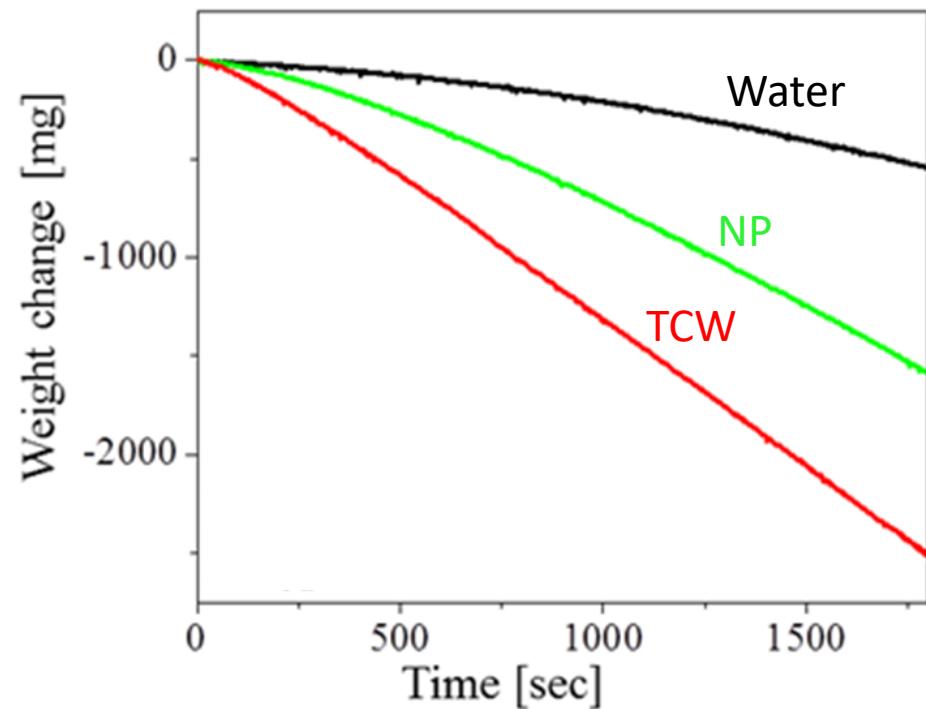
Ceramic
wool



TiN NPs
**Composite
(TCW)**



M. Kaur



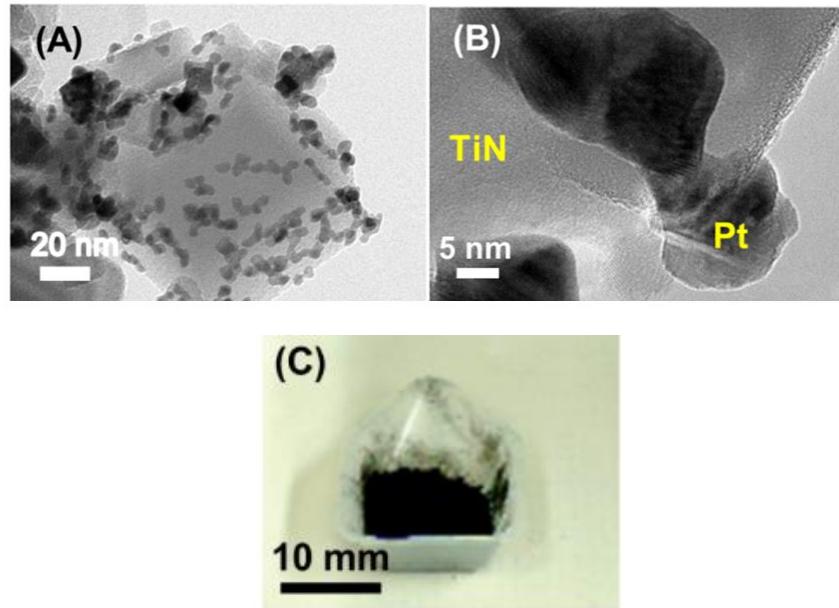
Capillary force of TCW
improved evaporation

M. Kaur, SI, et al, ACS Sustain. Chem. Eng. (2017)

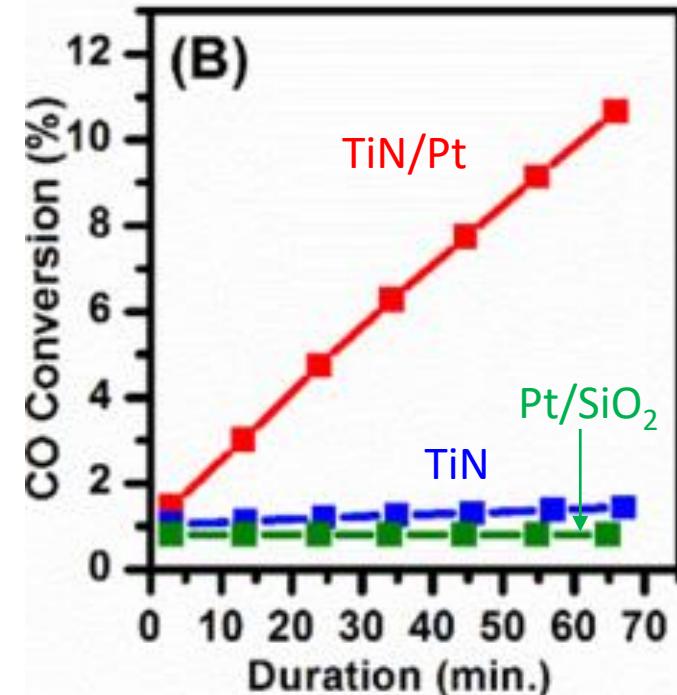
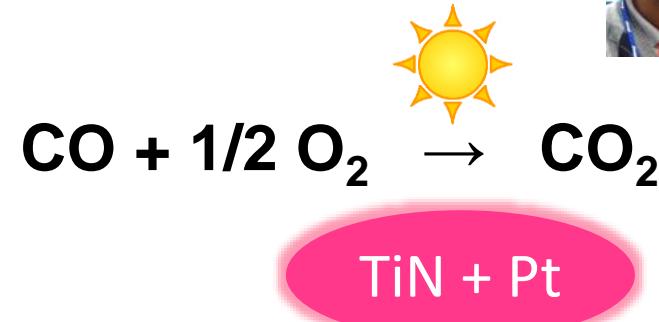
Photothermal chemical reaction

Oxidation of CO

- Conventional: heat >200 degC
- Ours: Pt-coated TiN NPs + focused sunlight



H. Abe &
O. Anjaneyulu



O. Anjaneyulu, S. Ishii, et al, RSC Adv. (2016)

Hot carrier engineering w/ TiN

