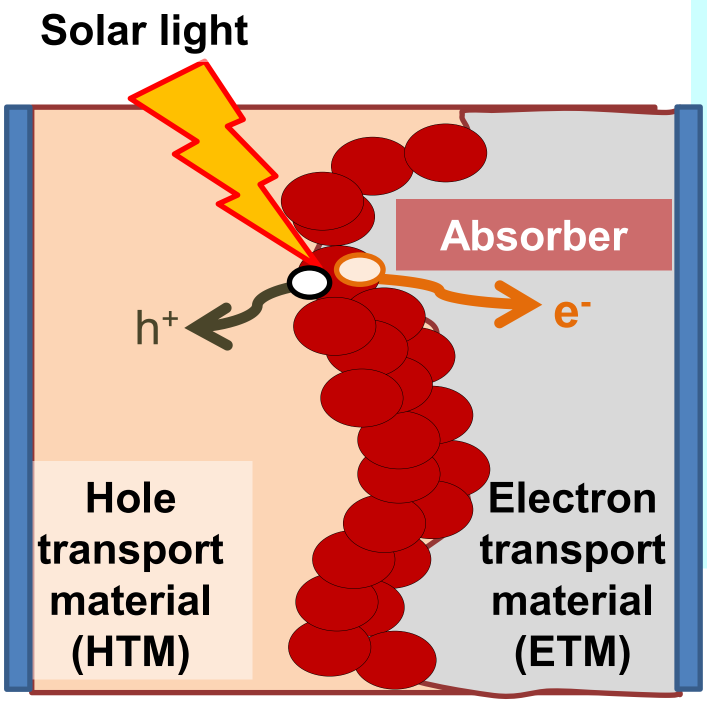
ペロブスカイト型の電荷ダイナミクス

沈　青

電気通信大学大学院理工学研究科　先進理工学専攻

Organic-Inorganic Hybrid Solar Cells



Schematic illustration of structure of an organic-inorganic hybrid solar cell (OIHSC)

Absorber
(dye, quantum dots (QDs), perovskite)

Efficiency of OIHSCs with different absorbers:

Dye: 1% (1998)[1] → 7.2% (2011)[2]

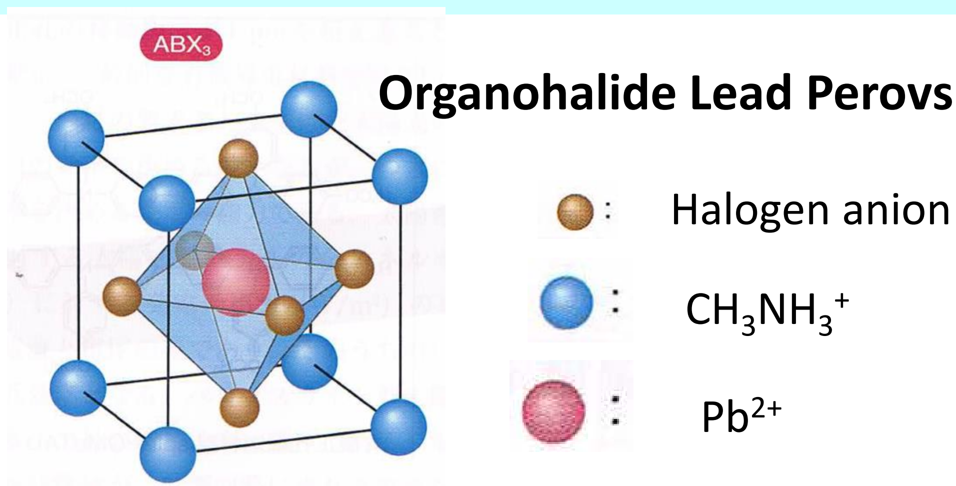
Improvements in absorption of dye and conductivity of HTM

Quantum dots (QDs): 5% (2010)[3] → 6.3% (2012)[4]

Sb_2S_3 and improvement in HTM

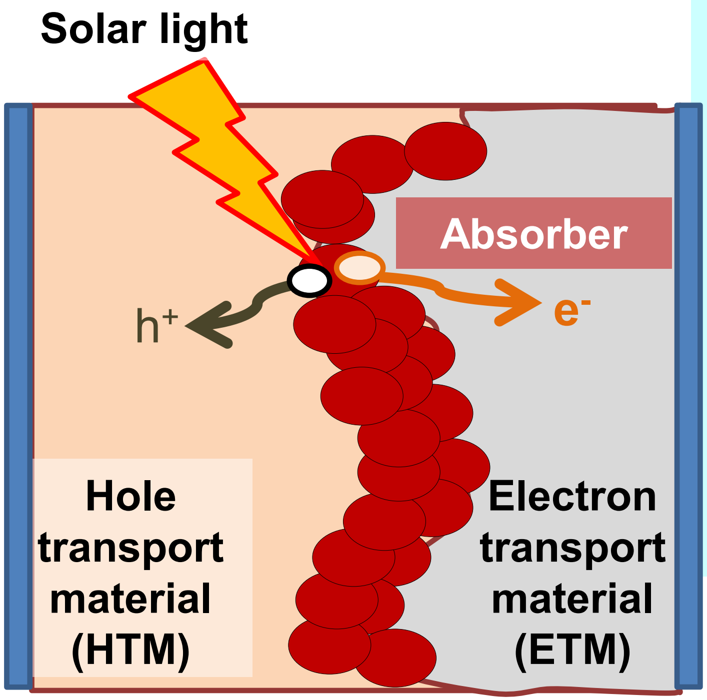
Perovskite lead iodide: 9.7% (2012)[5] → 20.1% (2014)[6]

Organohalide Lead Perovskites



1) M. Gratzel et al., Nature 1998, 395, 583−585.
2) M. Gratzel et al., J. Am. Chem. Soc. 2011, 133, 18042−18045.
3) S. I. Seok et al., Nano Lett. 2010, 10, 2609−2612.
4) S. I. Seok et al., Nano Lett. 2012, 12, 1863−1867.
5) N. G. Park et al., Sci. Rep. 2012, 2, 591.
6) http://www.nrel.gov/ncpv/

Organic-Inorganic Hybrid Solar Cells



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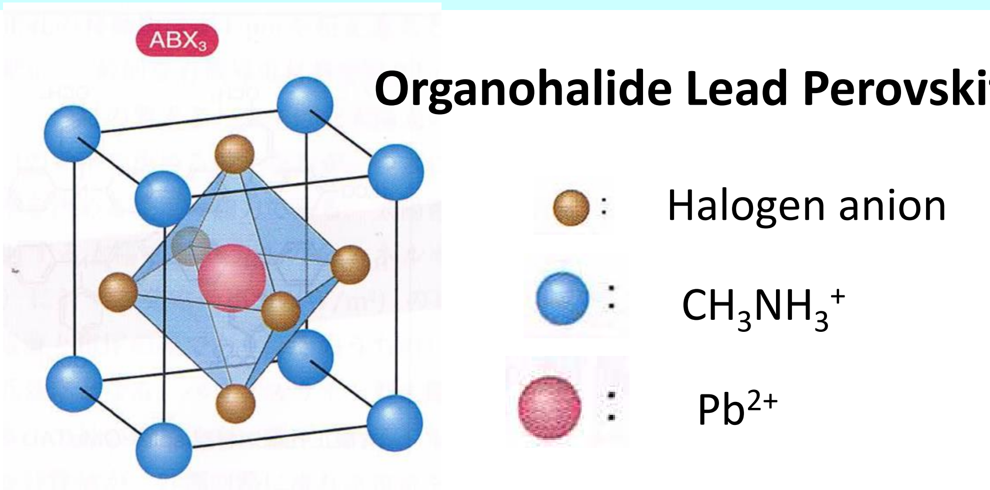

Why the efficiency of perovskite-based OIHSCs can be so high?

Unique properties of Pb perovskite for solid state solar cells

（1）high optical absorption coefficient

N719: α = 1500 cm^{-1} at 540 nm; $CH_3NH_3PbI_3$: α = 15000 cm^{-1} at 550 nm

（2）long electron and hole diffusion length in the perovskite

$CH_3NH_3PbI_3$: 100 nm; $CH_3NH_3PbI_{3-x}Cl_x$: > 1000 nm

S. D. Stranks et al., Sicence 342, 341 (2013); G. C. Xing et al., Science 342, 344 (2013).

longer lifetimes of photoexcited carriers in Pb perovskie

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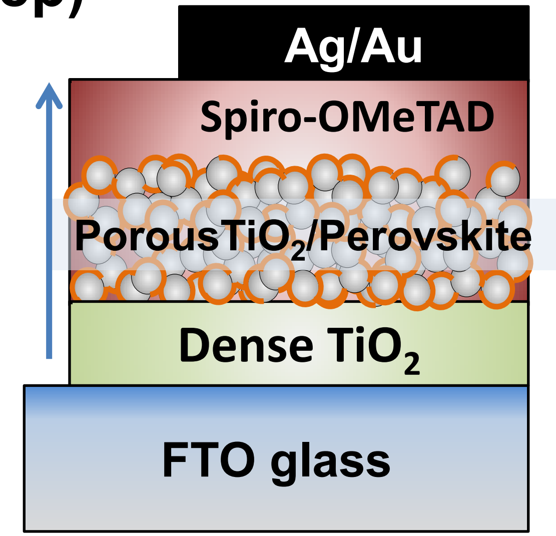
Some open questions for perovskite-based solar cells

1. What is the time scale of charge separation and recombination and which interface do they occur?
2. How about charge separation and charge collection efficiency?
3. How about surface engineering (surface passivation) influence charge separation and collection efficiency?

Our studies on Charge Separation and Recombination in Perovskite Solar cells

(1) $TiO_2/CH_3NH_3PbI_xCl_{3-x}I$ /Spiro-OmeTAD (one step)



◇ surface passivation of TiO_2 surface with Y_2O_3

ChemPhysChem, Vol. 15, 1062 (2014).

◇ Dependence on TiO_2 morphology

Phys. Chem. Chem. Phys., Vol. 16, 19984 (2014).

(2) $TiO_2/CH_3NH_3PbI_3$/Spiro-OmeTAD (two step)

◇ Interface engineering by inserting $HOCO\text{-}RNH_3{}^+I^-$ anchor group at Perovskite/TiO_2 interfaces

J. Phys. Chem. C, Vol. 118, 16651 (2014).

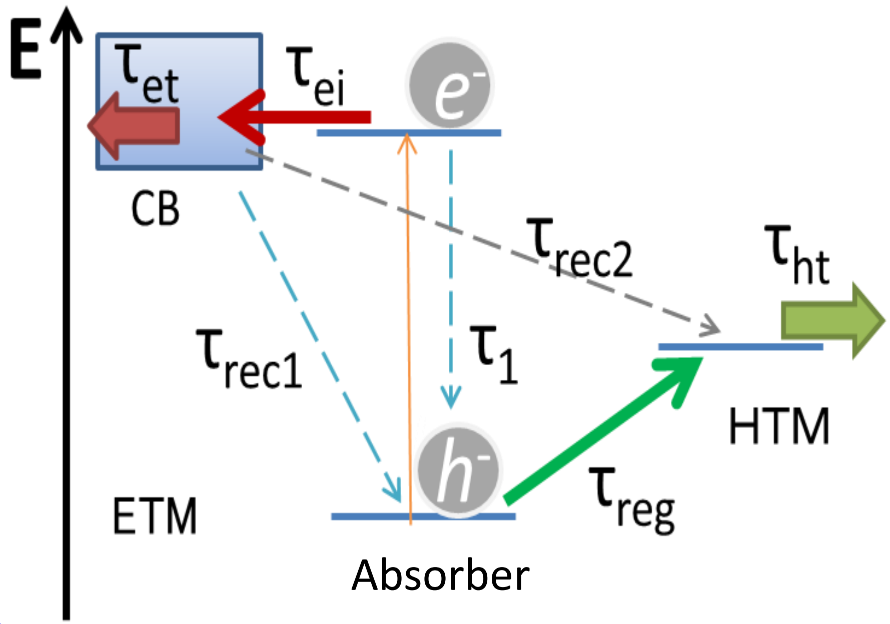
(3) $TiO_2/CH_3NH_3Sn_xPb_{1-x}I_3$ /Spiro-OmeTAD (one step)

◇ Carrier dynamics depends greatly on the ratio x of Sn and Pb

Submitted for publication

Charge Separation and Recombination in OIHSC

One Key for Improving the Efficiency

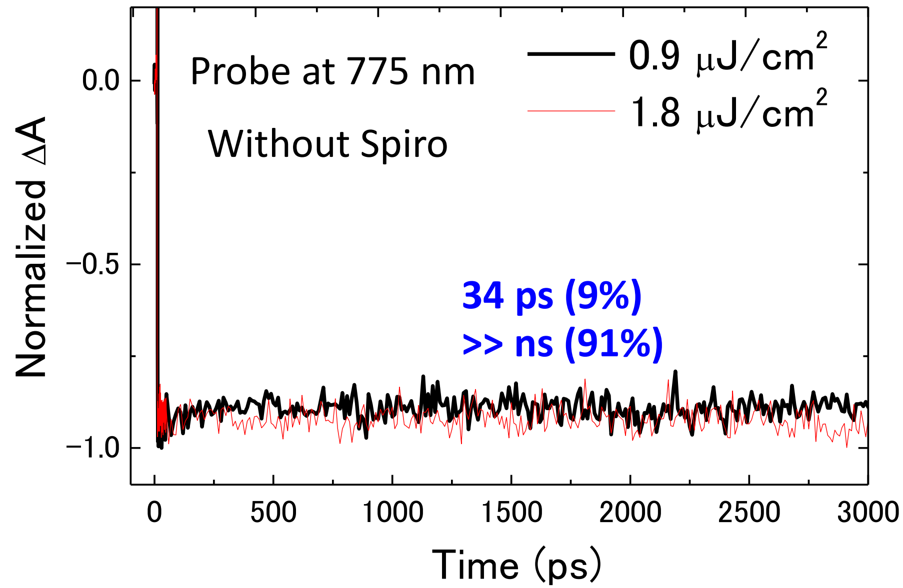


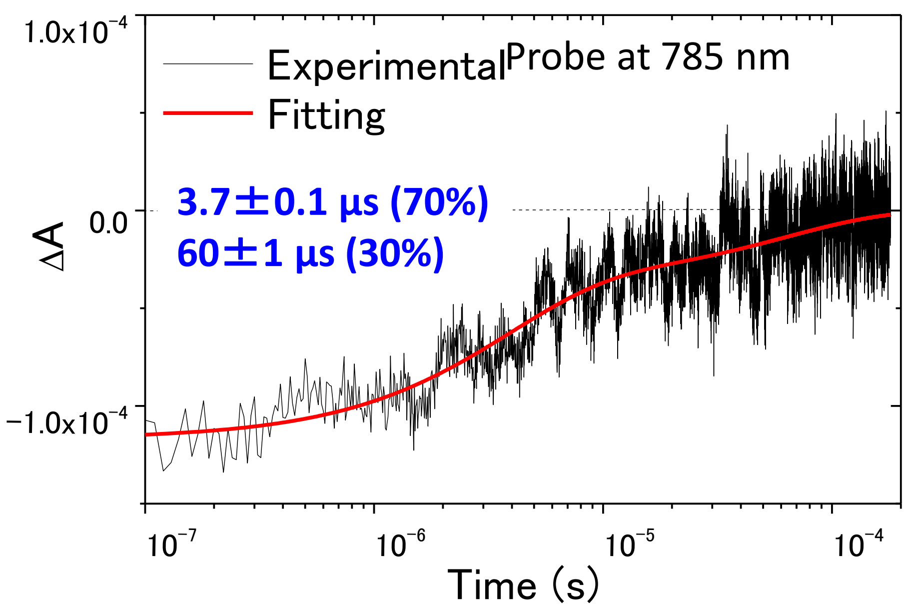
τ_{ei}: electron injection time;
τ_{reg}: hole transfer time
τ_1: life time of photoexcited electron-hole pairs
τ_{rec1}: recombination time of electrons in TiO_2 with holes in sensitizer
τ_{rec2}: recombination time of electrons in TiO_2 with holes in HTM
τ_{et}: electron transport time in ETM
τ_{ht}: hole transport time in HTM

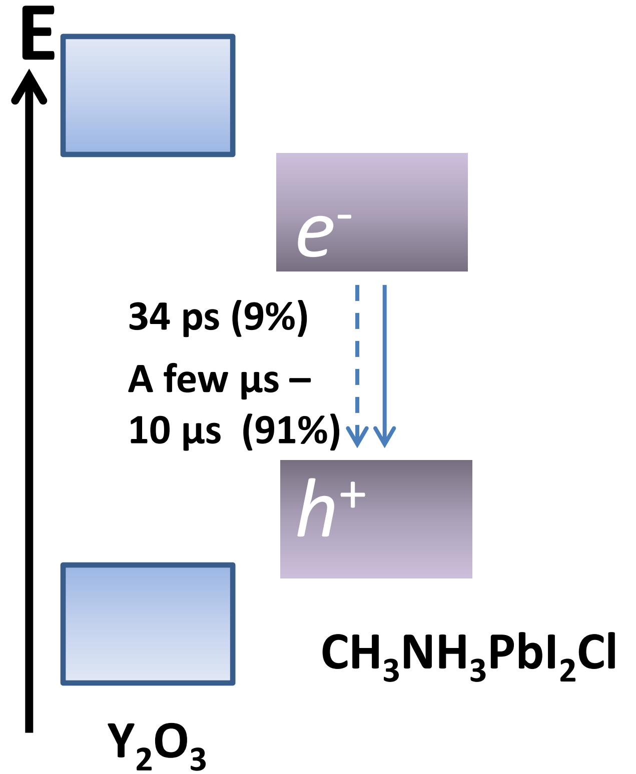
Exciton generation & diffusion | Charge separation & charge recombination | Charge transport

The charge separation and recombination dynamics from sub-picoseconds to milliseconds can be detected with a <u>transient absorption (TA) method</u>.

Recombination in $CH_3NH_3PbI_xCl_{3-x}$ on Y_2O_3





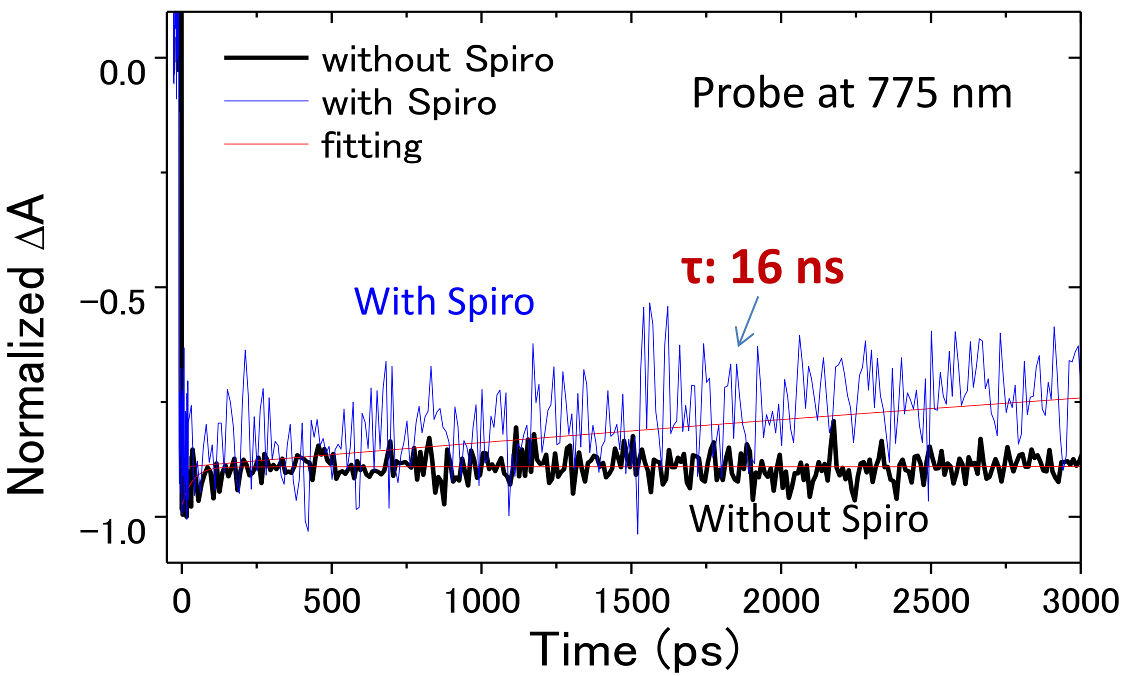


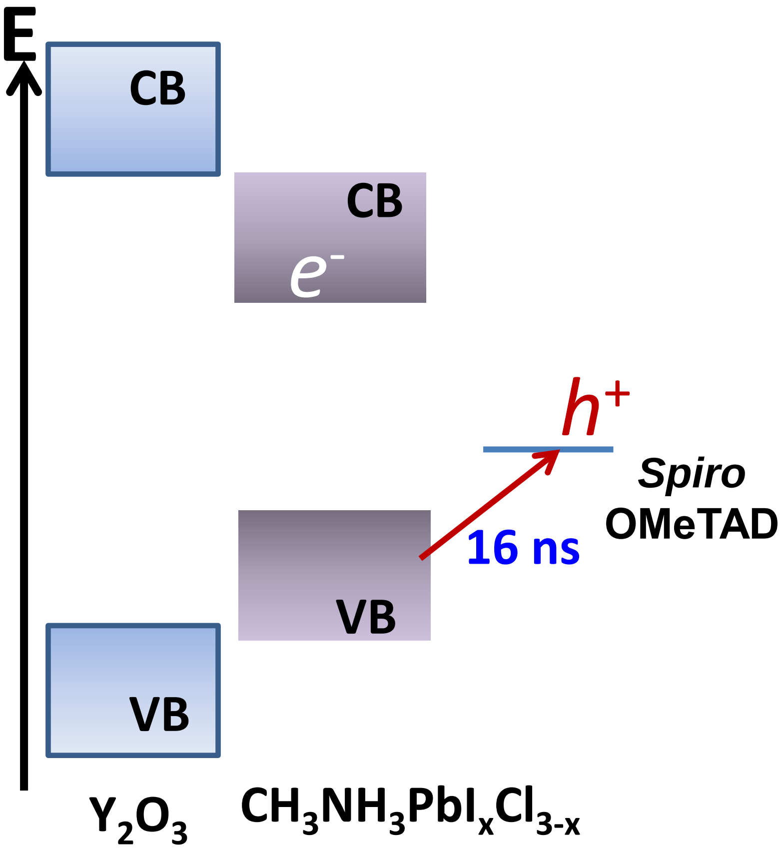
Three recombination processes:
(1) 34 ps (9%)
(2) 3.7 μs (64%)
(3) 60 μs (27%)

ChemPhysChem, Vol. 15, 1062 (2014).

Phys. Chem. Chem. Phys., Vol. 16, 19984

Charge separation at $CH_3NH_3PbI_xCl_{3-x}$ / *Spiro*-OMeTAD interface





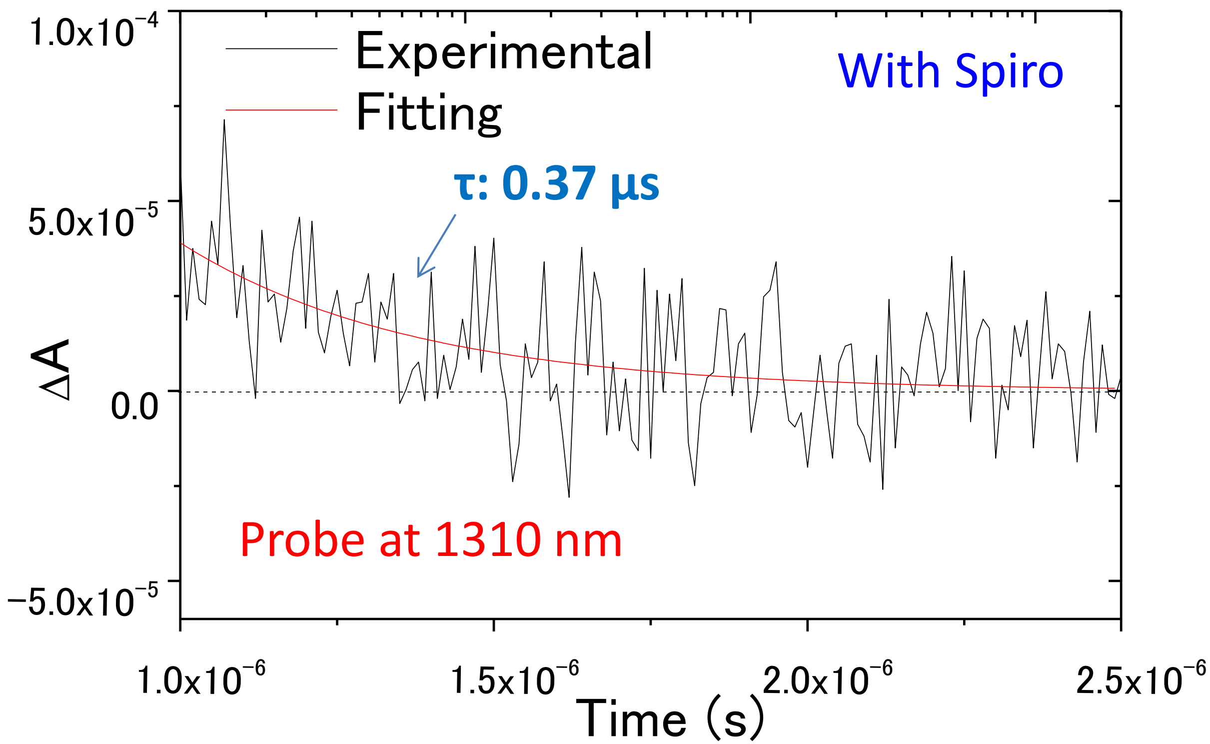
There is charge separation at $CH_3NH_3PbI_xCl_{3-x}$/ *Spiro*-OMeTAD interface

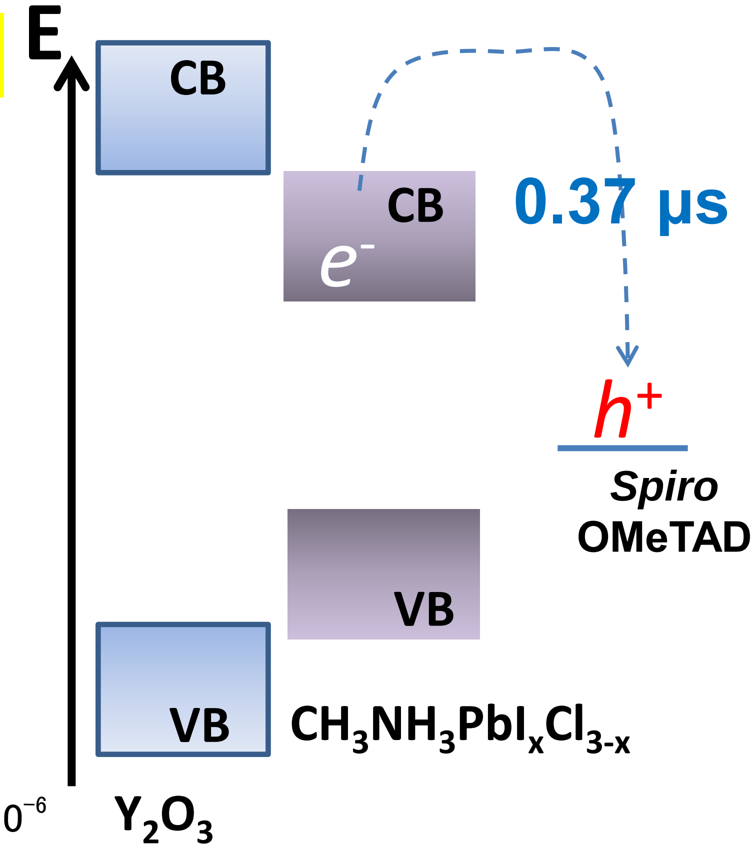
Hole injection time: 16 ns

Phys. Chem. Chem. Phys., Vol. 16, 19984 (2014).

charge recombination at $CH_3NH_3PbI_xCl_{3-x}$ /*Spiro*-OMeTAD interface

Probe light : 1310 nm ⟶ Monitor holes in Spiro



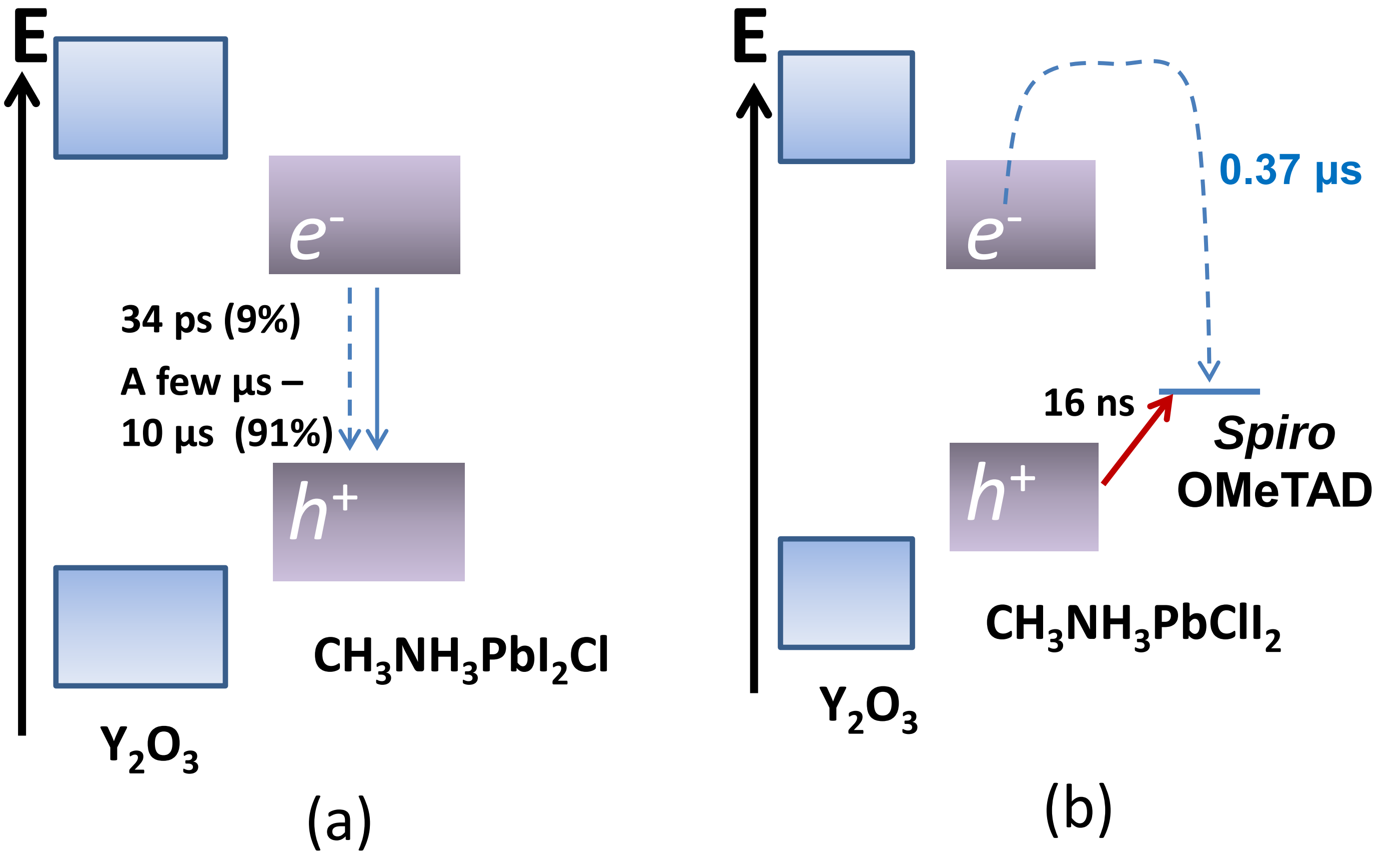


There is charge separation at $CH_3NH_3PbClI_2$/ *Spiro*-OMeTAD interface

Recombination time: 0.37 μs

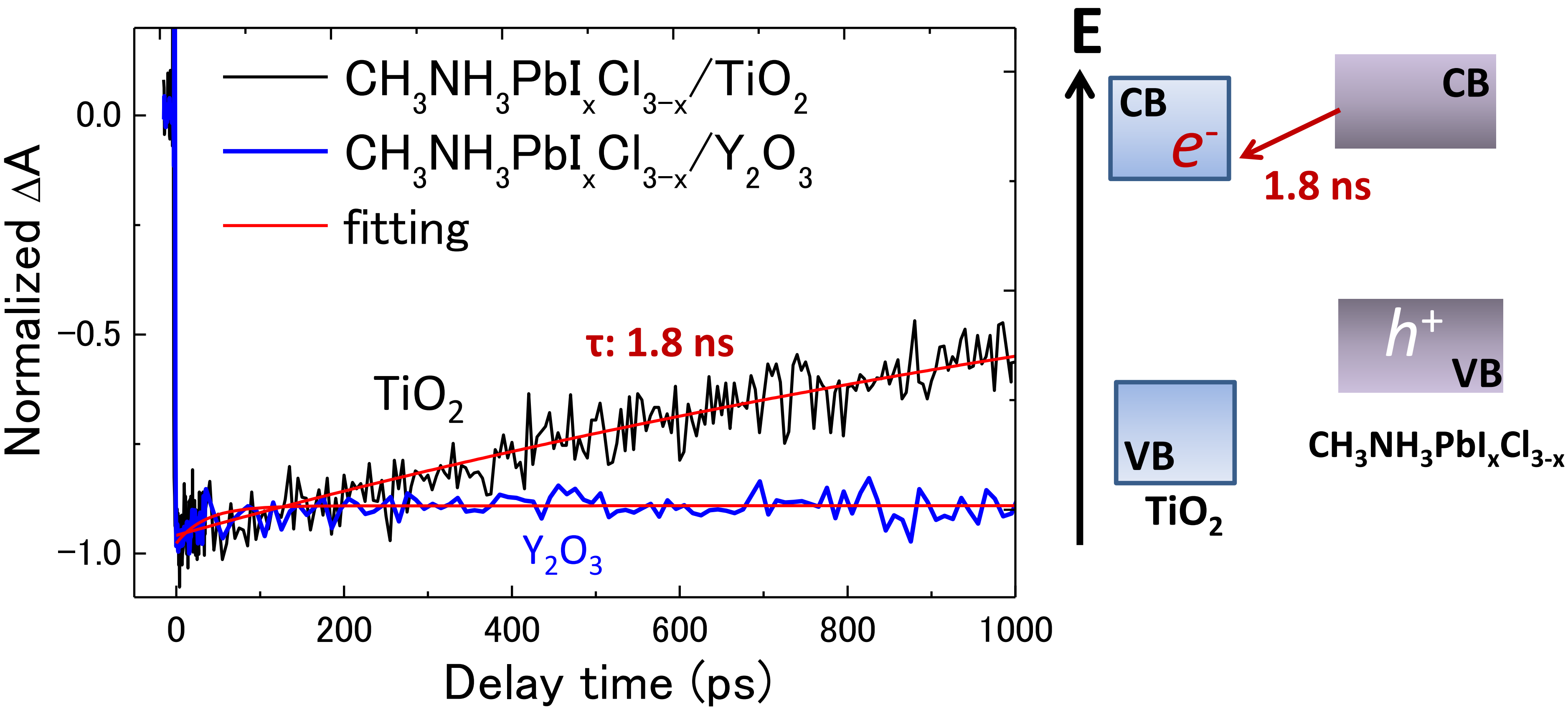
Phys. Chem. Chem. Phys., Vol. 16, 19984 (2014).

Charge separation and recombination at $CH_3NH_3PbI_xCl_{3-x}$ / *Spiro*-OMeTAD interface on Y_2O_3



Phys. Chem. Chem. Phys., Vol. 16, 19984 (2014).

Charge separation at $CH_3NH_3PbI_xCl_{3-x}/TiO_2$ interface

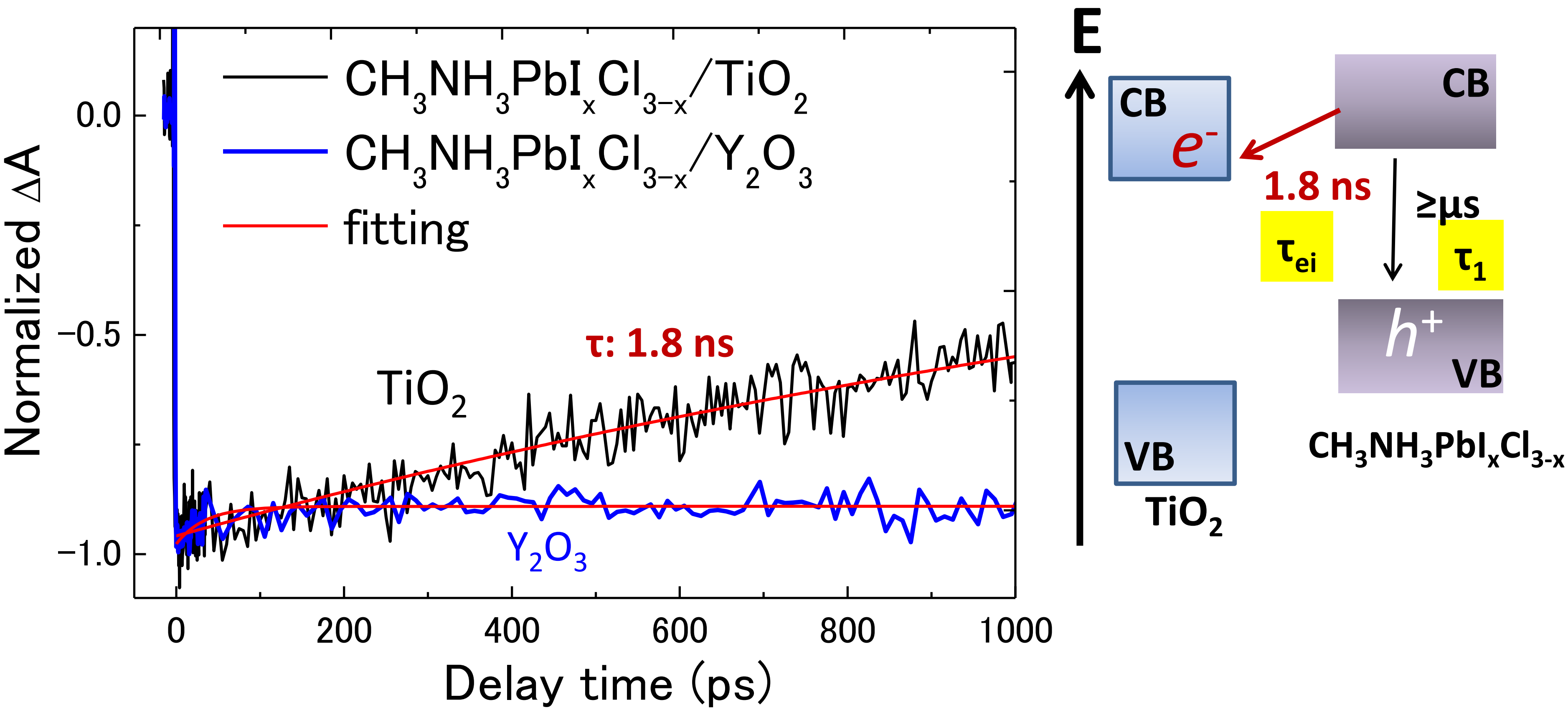


There is electron injection from $CH_3NH_3PbI_xCl_{3-x}$ to TiO_2.

ChemPhysChem, Vol. 15, 1062 (2014).

Phys. Chem. Chem. Phys., Vol. 16, 19984 (2014).

Charge separation at $CH_3NH_3PbI_xCl_{3-x}/TiO_2$ interface



Electron injection efficiency η_{ET}

Phys. Chem. Chem. Phys., Vol. 16, 19984 (2014).

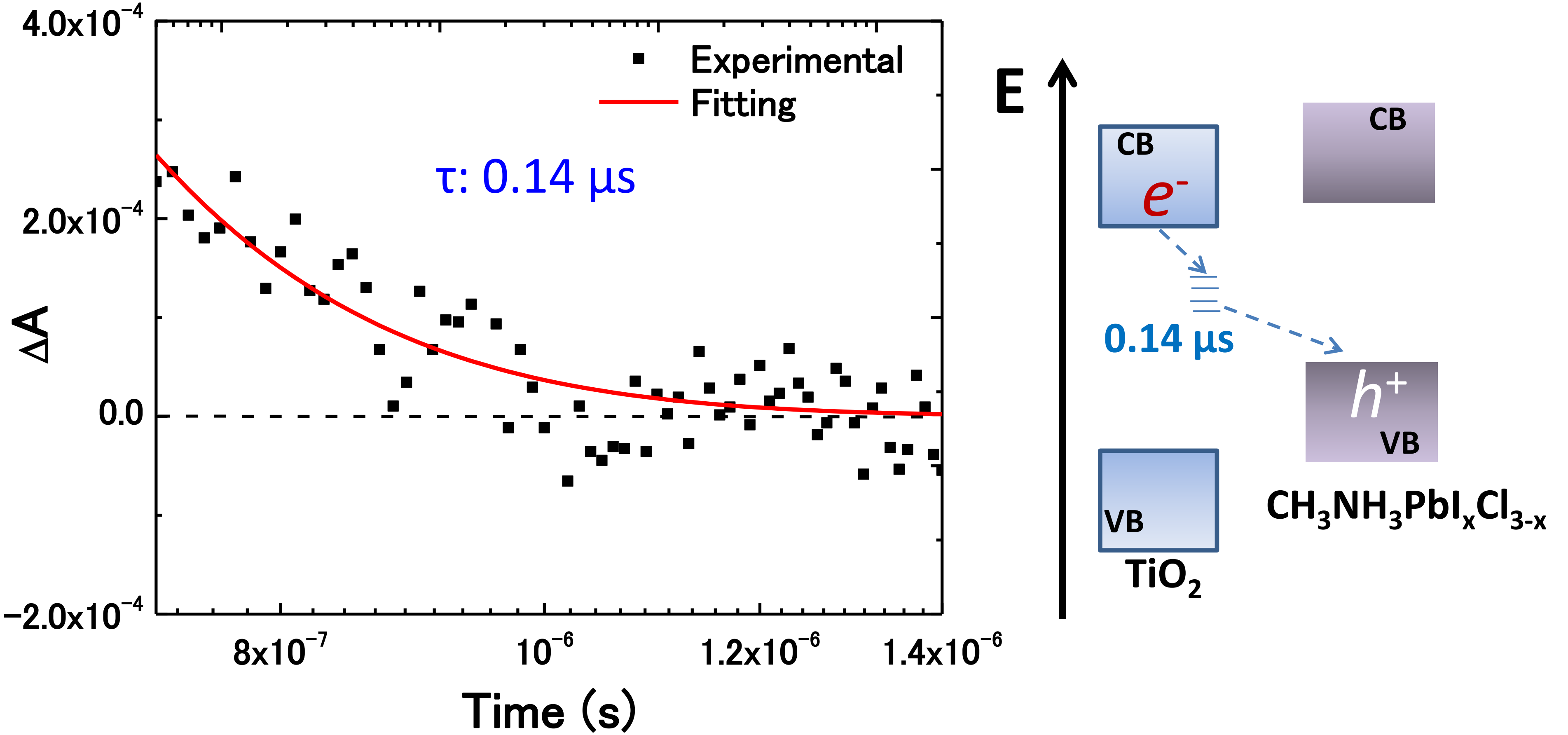
$$\eta_{ET} = (1/\tau_{ei})/(1/\tau_{ei}+1/\tau_1)$$

η_{ET}: close to 100%

Charge recombination at $CH_3NH_3PbI_xCl_{3-x}/TiO_2$ interface

Probe light wavelength: 658 nm ➡ Monitor electrons in TiO_2

T. Yoshihara et al., *The Journal of Physical Chemistry B*, 2004, **108**, 3817-3823.
Physical Chemistry Chemical Physics, 2014, **16**, 5242; 2013, **15**, 11006; 2014, **16**, 5774.



ChemPhysChem, Vol. 15, 1062 (2014).

Phys. Chem. Chem. Phys. (2014). DOI: 10.1039/C4CP03073G.

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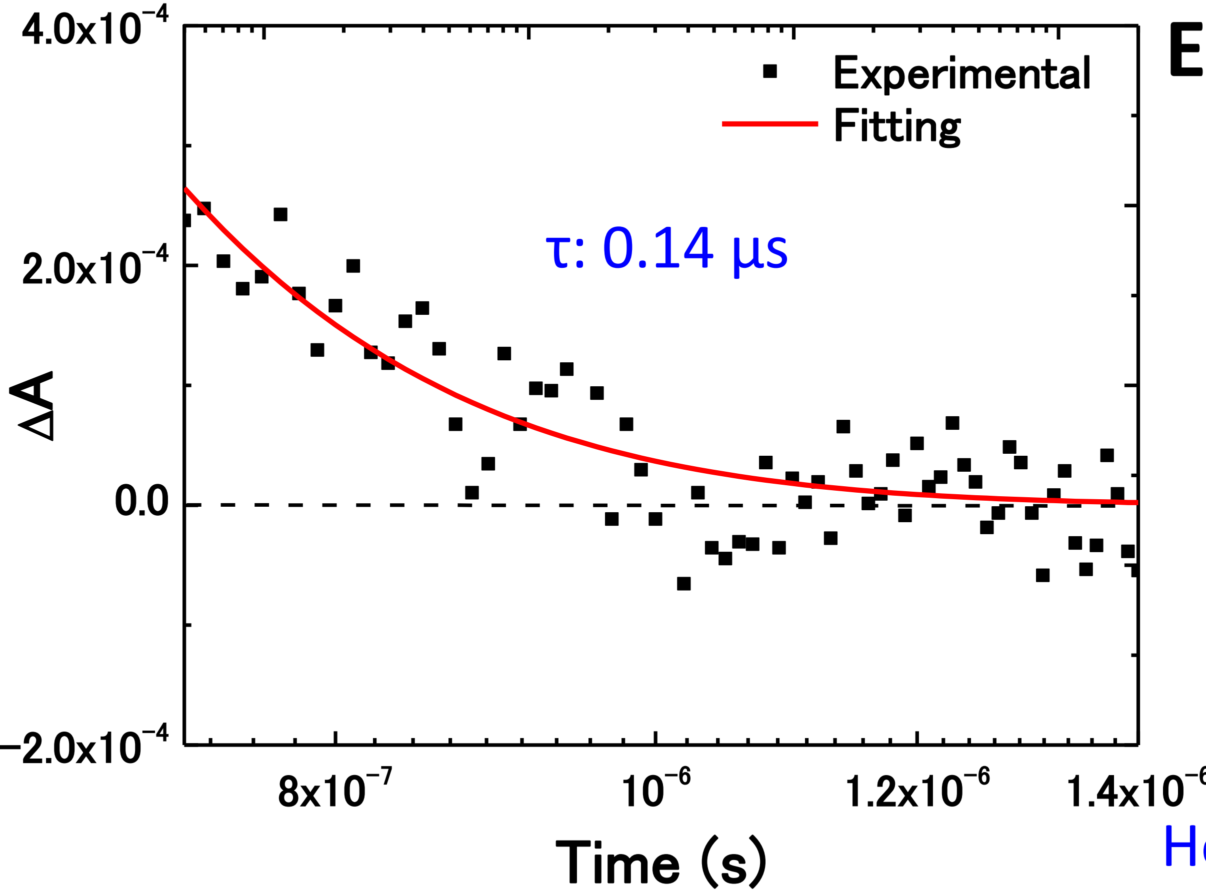
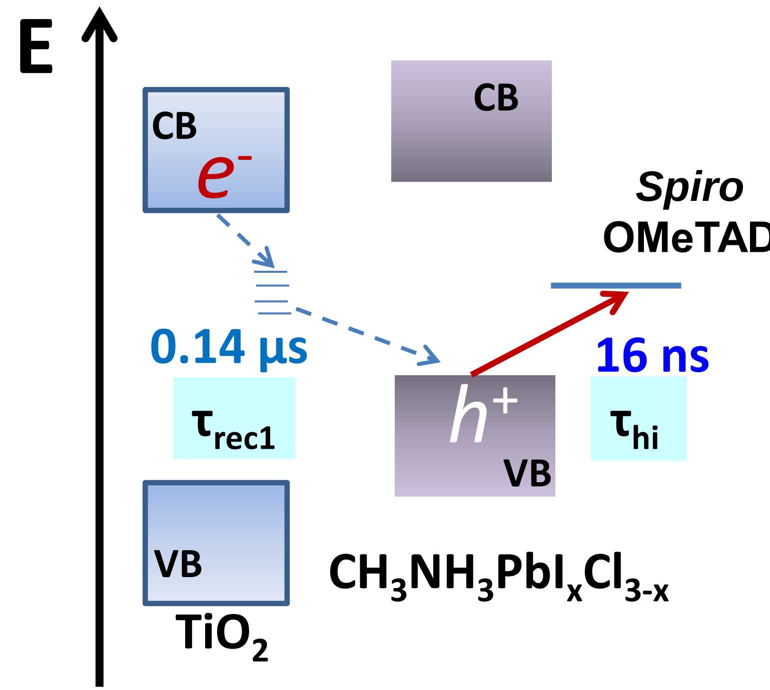




Hole injection efficiency η_{HT}

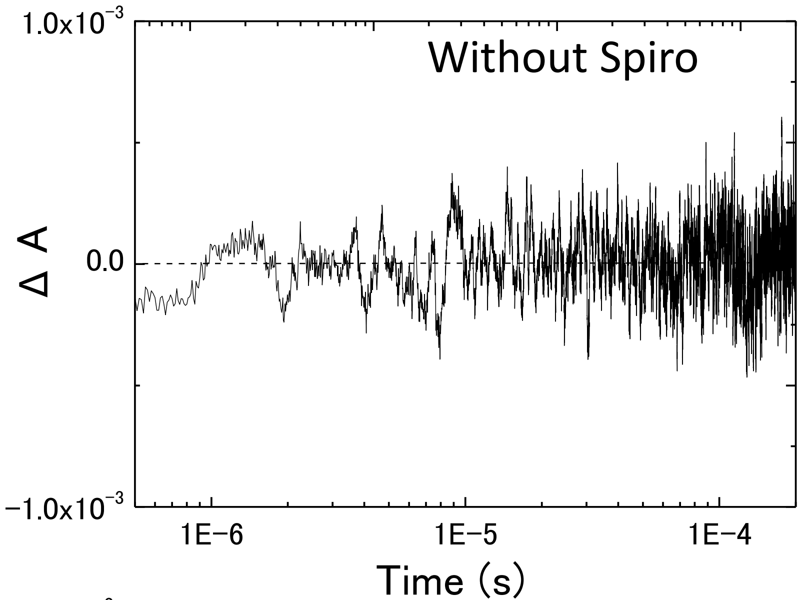
$\eta_{HT} = (1/\tau_{hi})/(1/\tau_{hi} + 1/\tau_{rec1})$

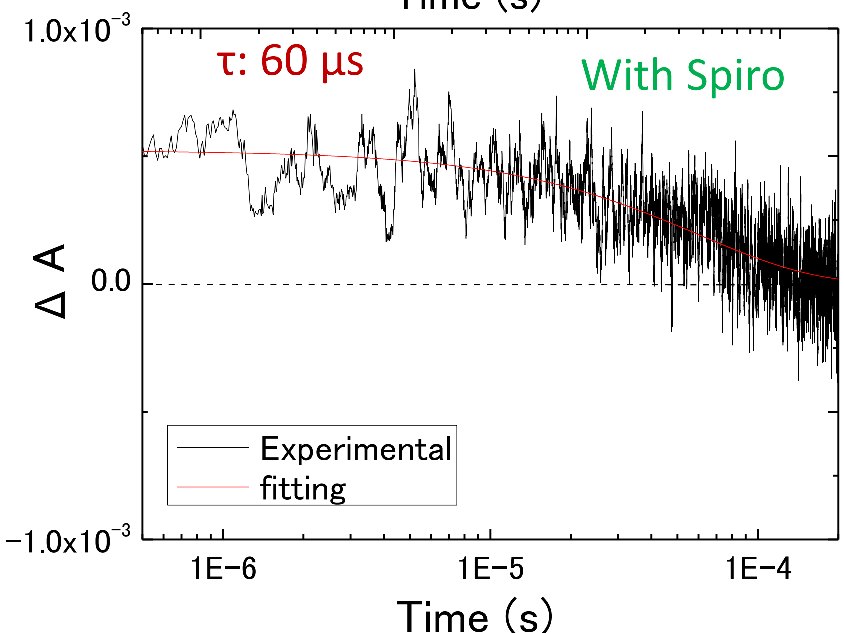
η_{HT}: about 90%

Charge separation efficiency: $\eta_{CS} = \eta_{ET}\,\eta_{HT} \approx 90\%$

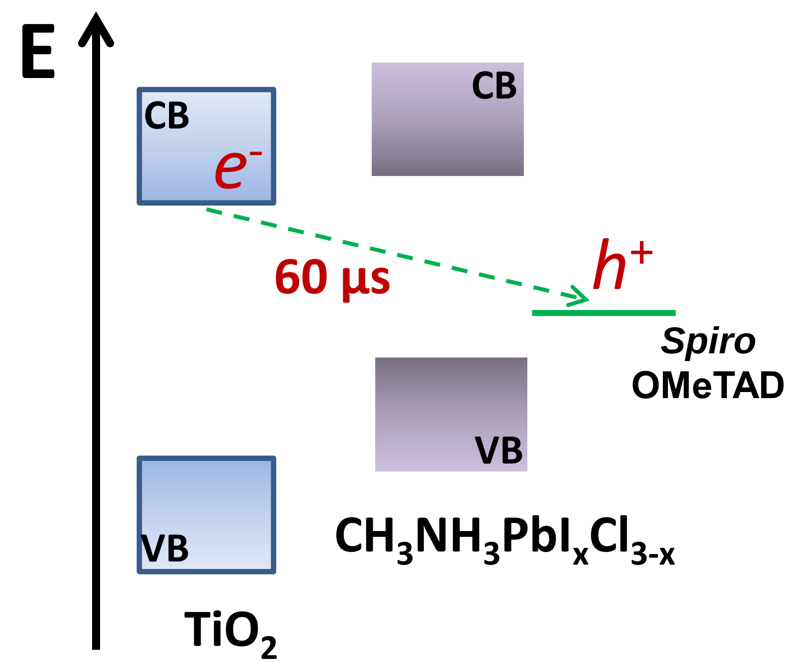
Charge recombination at TiO_2/*Spiro*-OMeTAD interface

Probe light wavelength: 1310 nm ➡ Monitor lifetime of holes in Spiro





R. Plass et al., *J. Physical Chemistry B*, 2002, **106**, 7578.



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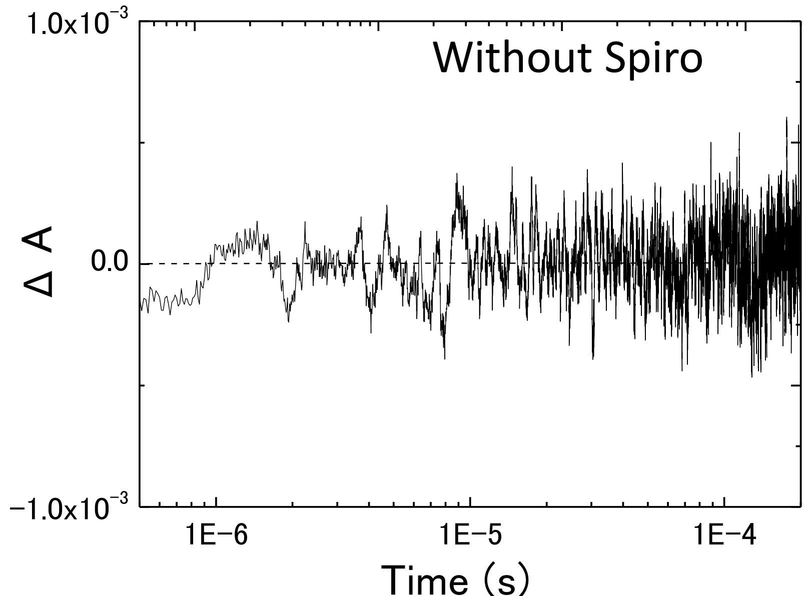
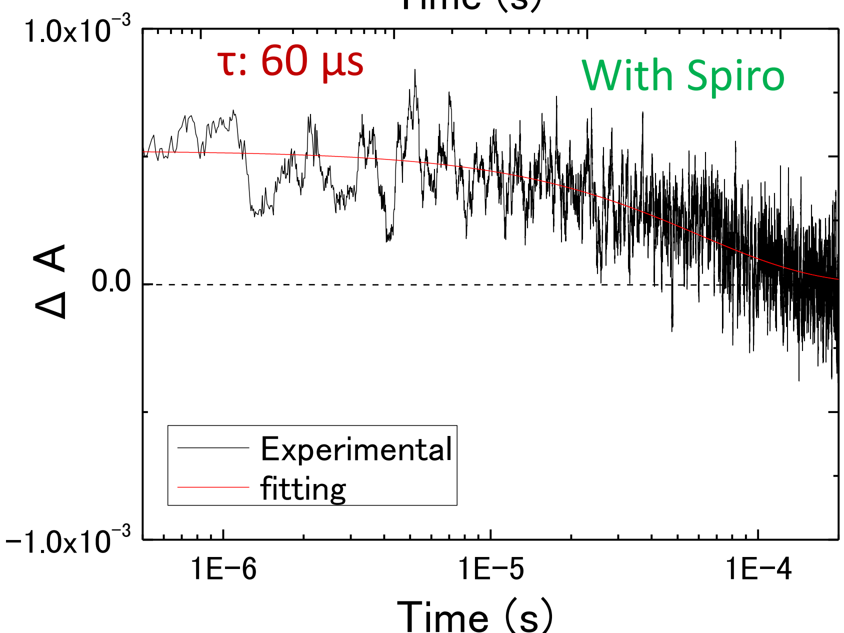
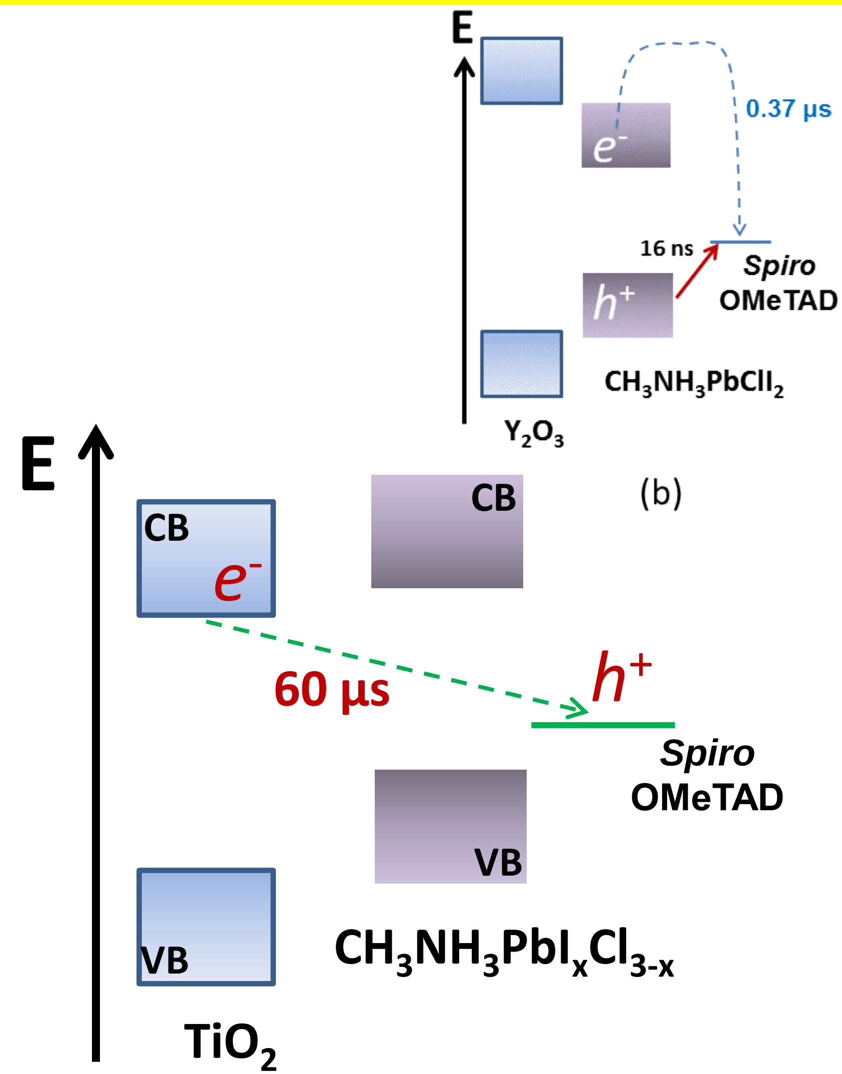
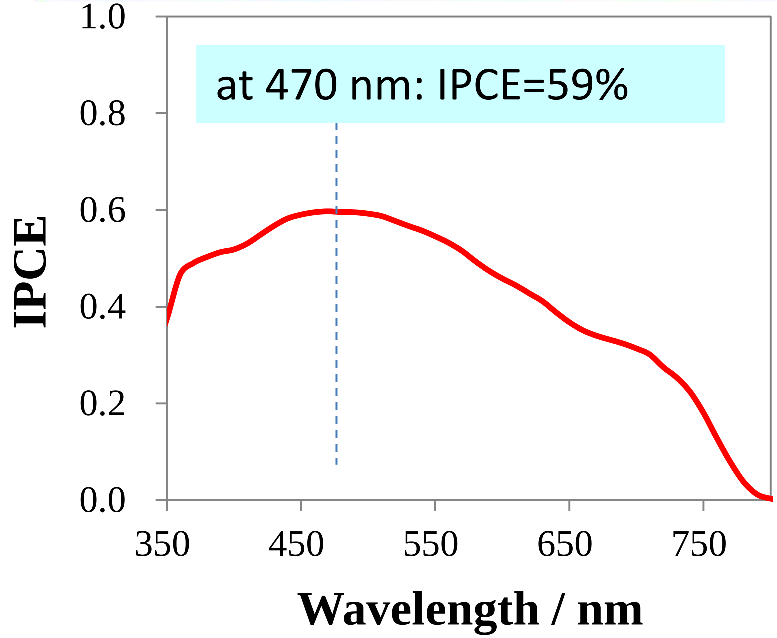


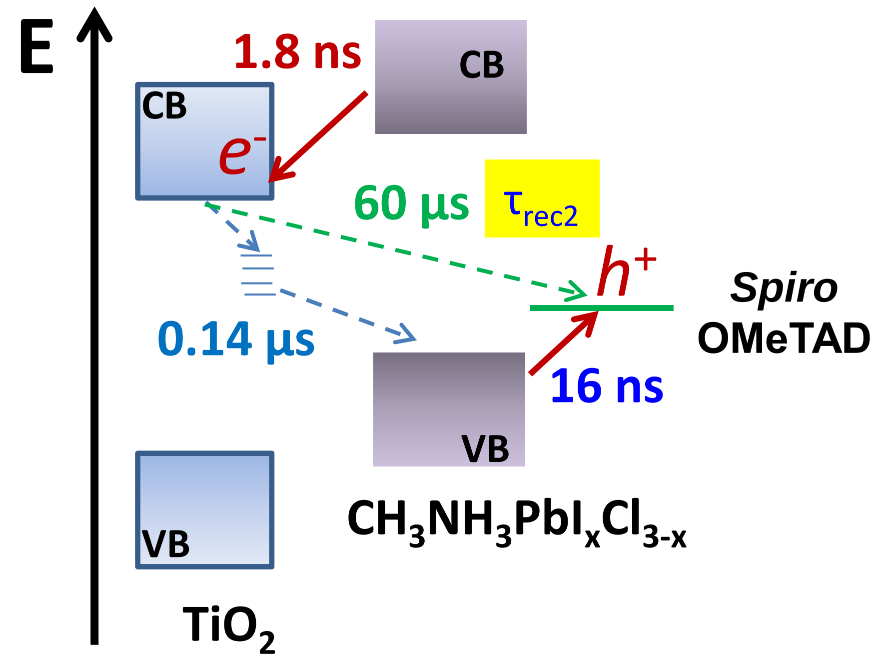


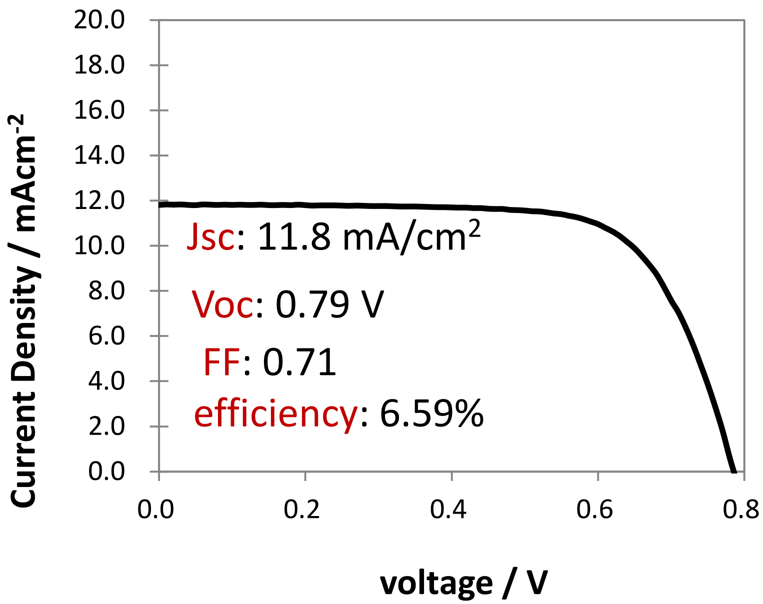


Phys. Chem. Chem. Phys., Vol. 16, 19984 (2014).

Relationship between Carrier Dynamics and Photovoltaic Performance







$$\mathrm{IPCE} = \eta_{absorption}\ \eta_{CS}\ \eta_{CC}$$

$\eta_{absorption} \approx 95\%$

$\eta_{CS} = \eta_{ET}\ \eta_{HT} \approx 90\%$

$\eta_{CC} < 70\%$

The problem: smaller τ_{rec2} ➡ smaller η_{CC}.

Phys. Chem. Chem. Phys., Vol. 16, 19984 (2014).

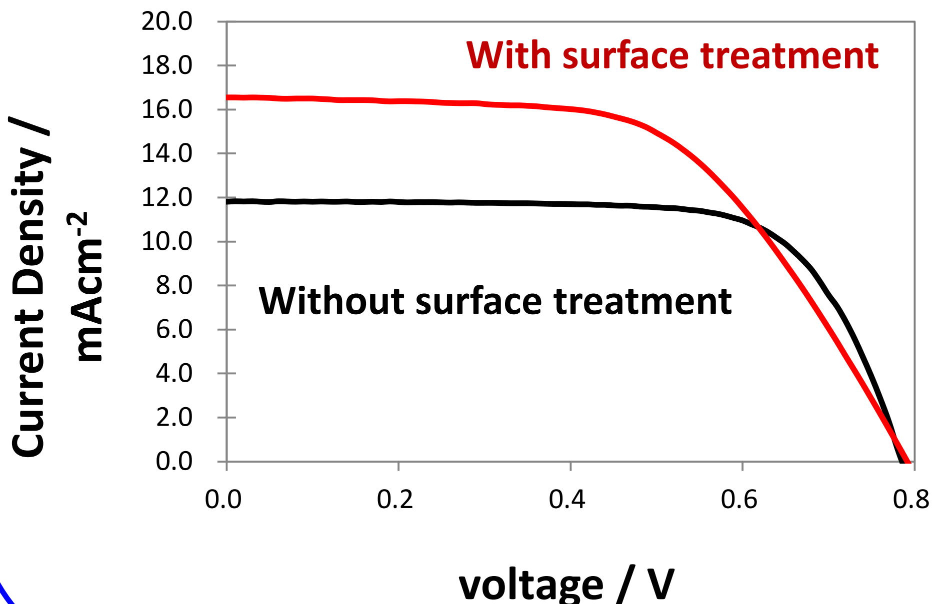
Effects of surface treatment on carrier dynamics and photovoltaic performance

After surface treatment of TiO_2

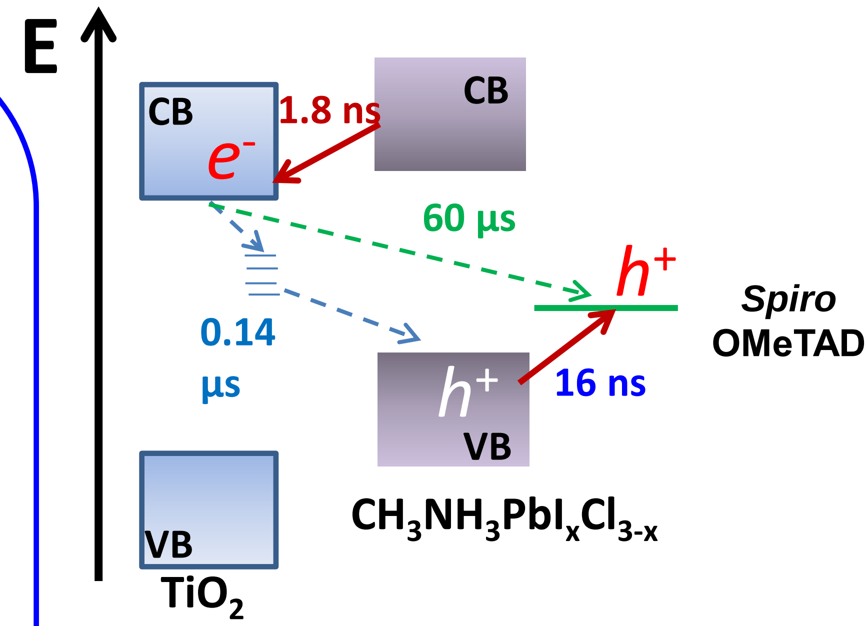
τ_{rec2}: 60 μs → **180 μs**

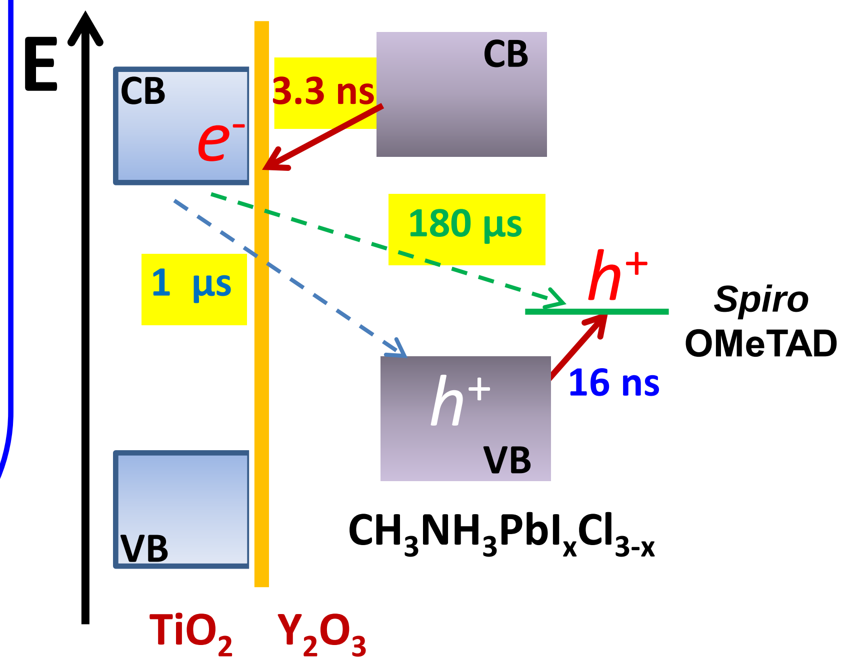
Jsc: 11.8 mA/cm² → 16.5 mA/cm²;

efficiency: 6.59% → 7.53%



ChemPhysChem, Vol. 15, 1062 (2014)





Effects of TiO_2 nanoparticle sizes on carrier dynamics and Photovoltaic Performance

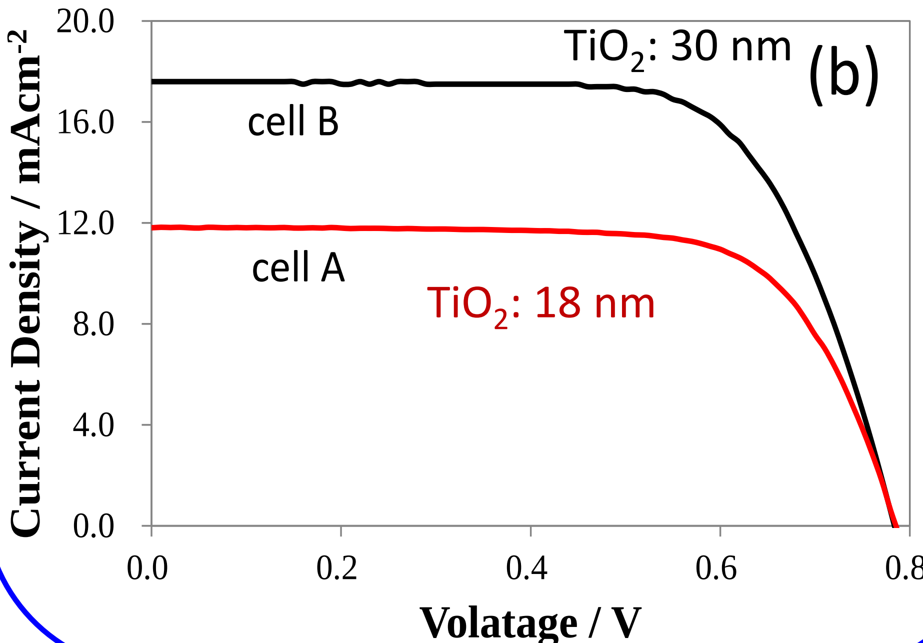
TiO_2 size: 18 nm → 30 nm

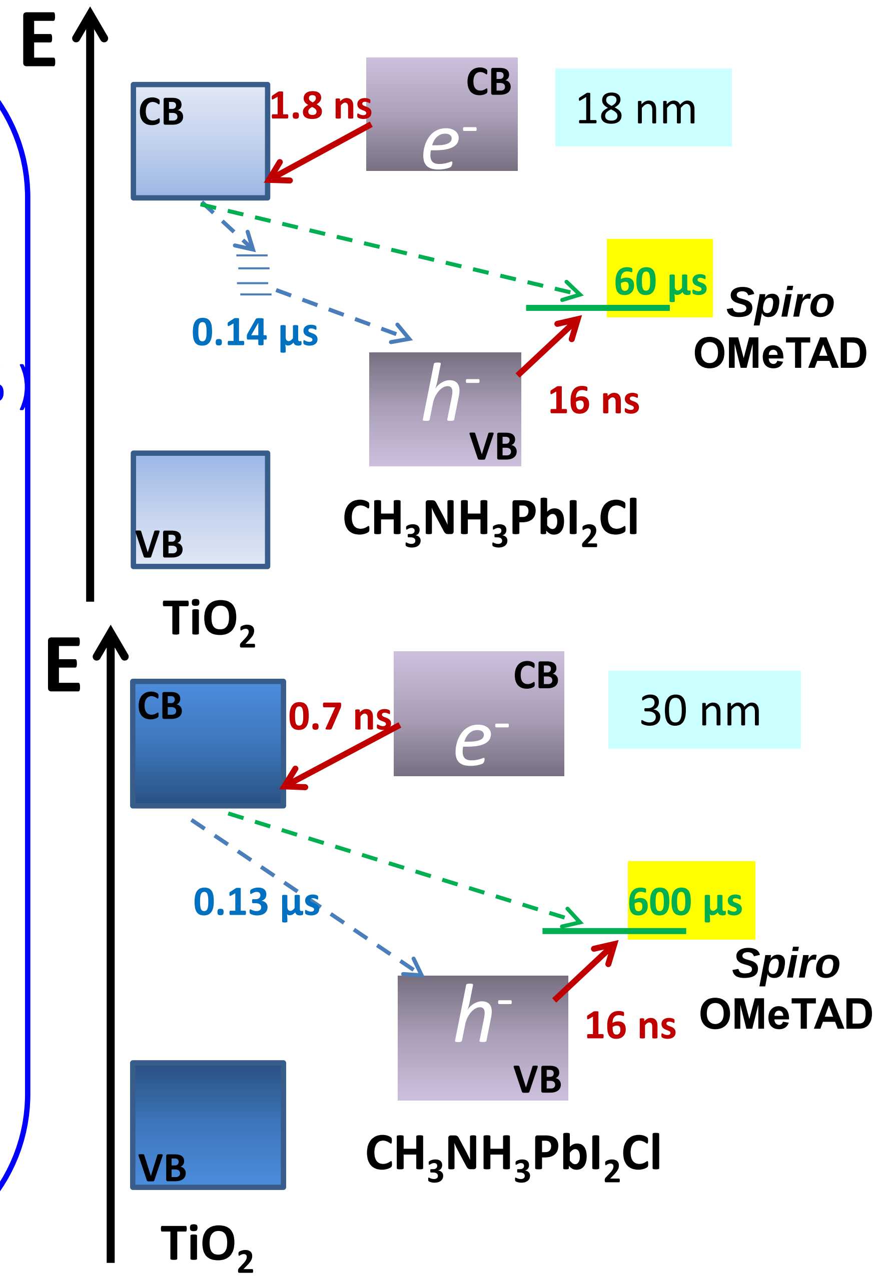
τ_{rec2}: 60 µs → 600 µs

IPCE(at 470nm):59% → 85% (η_{CC} ≈ 100%)

Jsc: 11.8 mA/cm² → 17.6 mA/cm²;

efficiency: 6.59% → 9.54%





Summary

(1) The carrier lifetime of perovskite $CH_3NH_3PbI_xCl_{3-x}$ is as large as μs.

(2) Charge separation efficiency is as high as 90% for $TiO_2/CH_3NH_3PbI_xCl_{3-x}$/*Spiro* OMeTAD.

(3) The key factor for improving the efficiency is to decrease the recombination at TiO_2/*Spiro* OMeTAD interface, which resulted in a smaller charge collection efficiency.

How to suppress the recombination is a key and surface passivation of TiO_2 and interface engineering are important.

Acknowledgment

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宮崎大学:吉野賢二先生
電通大:豊田太郎先生