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Hydrogen Production by Photocatalytic Water Splitting over Pt/TiO2 Nanosheets with Exposed (001) Facets

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TiO2 (001)에 대해 이해하기 좋은 논문입니다.
간략하게 요약하였습니다…..

1. Experiment

$Ti(OC_4H_9)_4$ (25ml) + HF (40 wt %, 3ml)

↓

Mixed in Autoclave at 25℃

↓

Hydrothermal treatment at 180℃ for 24hours

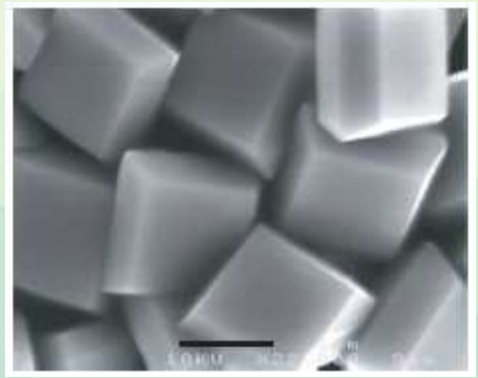
↓

White precipitate was collected by centrifuge and washed

↓

Dry at 80℃ for 6hours

TiO2 Single Crystal Nanosheet exposed on (001)



Pt coated TiO2 Nanosheet exposed on (001)

TiO2 Nanosheet powders (0.2g) + H2PtCl6 solution (80ml)

↓

Suspensions were stirred UV illumination for 20 min at 25℃

↓

precipitate was collected by centrifuge and washed

↓

Dry at 80℃ for 12hours

TABLE 1: Experimental Conditions for the Preparation of Samples

no.	R_F	morphology	phase[a]	R_{Pt}	washing	composition	color
NS1	1	nanosheets	A	0	no	TiO_2/F	white
NS2	1	nanosheets	A	0.5	no	TiO_2/F/Pt	light gray
NS3	1	nanosheets	A	1	no	TiO_2/F/Pt	light gray
NS4	1	nanosheets	A	2	no	TiO_2/F/Pt	gray
NS5	1	nanosheets	A	4	no	TiO_2/F/Pt	black
NS6	1	nanosheets	A	6	no	TiO_2/F/Pt	black
NS7	1	nanosheets	A	2	yes	TiO_2/Pt	gray
P25	0	nanoparticles	A, R	2	no	TiO_2/Pt	gray
NP	0	nanoparticles	A	2	no	TiO_2/Pt	gray

[a] A and R denote anatase and rutile, respectively.

R_F: molar ratios of HF to $Ti(OC_4H_9)_4$

R_{Pt}: weight ratios of Pt to Ti

Cleaned with 0.1M NaOH solution

TiO2 Nanosheets

Yang, H. G.; Sun, C. H.; Qiao, S. Z.; Zou, J.; Liu, G.; Smith, S. C.; Cheng, H. M.; Lu, G. Q. *Nature* ***2008, 453, 638.***

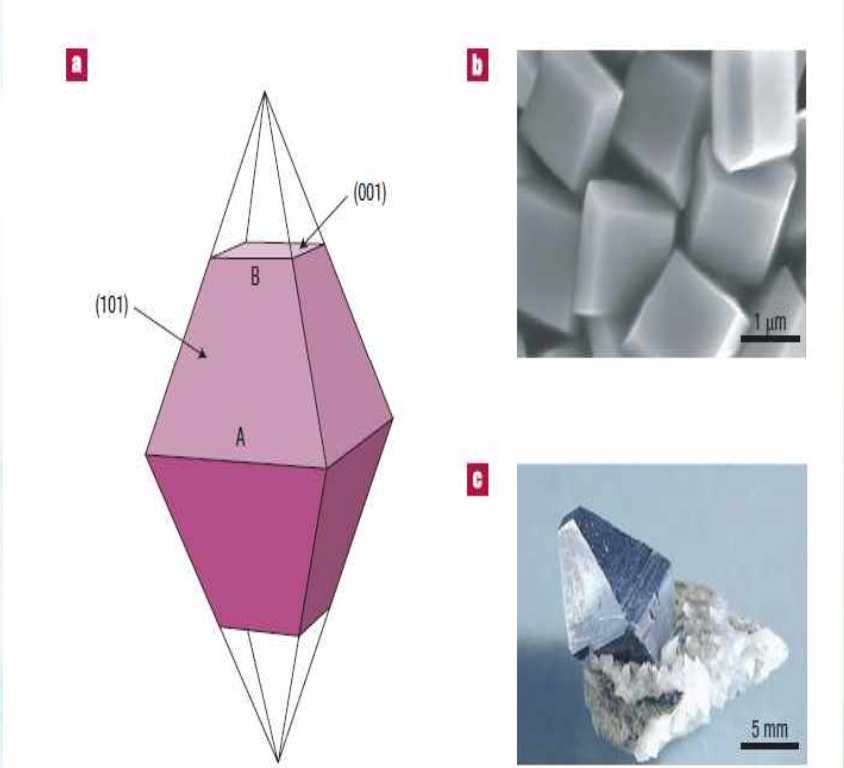


Figure 1 Facets of anatase TiO_2. **a**, The truncated tetragonal bipyramid crystal form, showing the {001} and {101} facets. A and B define the aspect ratio. **b**, The crystals with large {001} facets made by Lu and co-workers[3]. **c**, An anatase crystal with a more usual aspect ratio and much larger {101} facets (reprinted from ref. 15 with permission from Elsevier, © 2003).

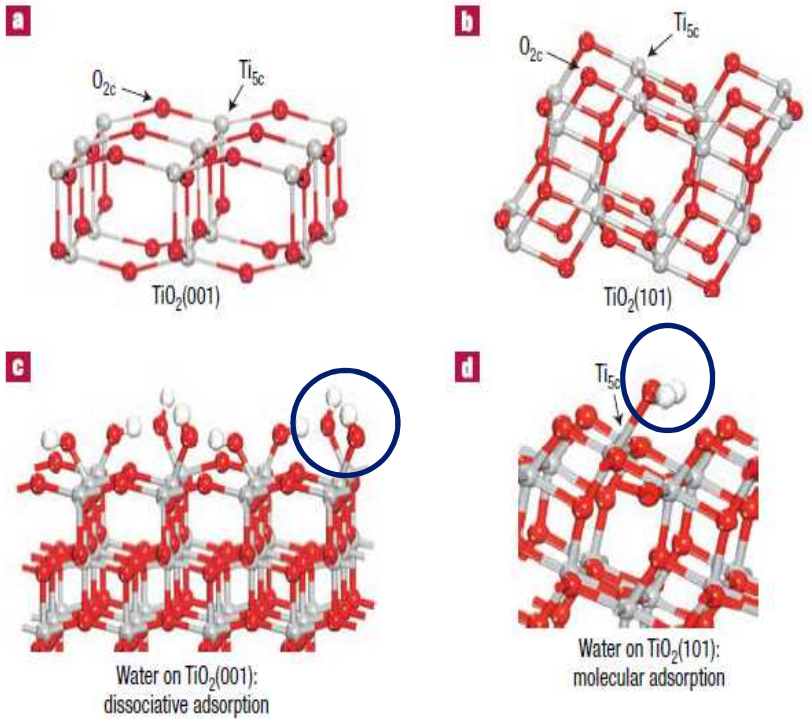


Figure 2 The atomic structure of anatase TiO_2 (001) and (101) surfaces and their water-adsorption behaviour. **a**, The more-reactive (001) surface showing strained Ti–O–Ti bond angles. O_{2c} and Ti_{5c} denote surface two-fold coordinated O atoms and five-fold coordinated Ti atoms, respectively. **b**, The less-reactive (101) surface. **c**, Water adsorbing dissociatively to the (001) surface. **d**, Water adsorbing to the (101) without dissociating.

Average side length of 50~80nm, thickness 6nm

Lattice spacing parallel to the top and bottom facets

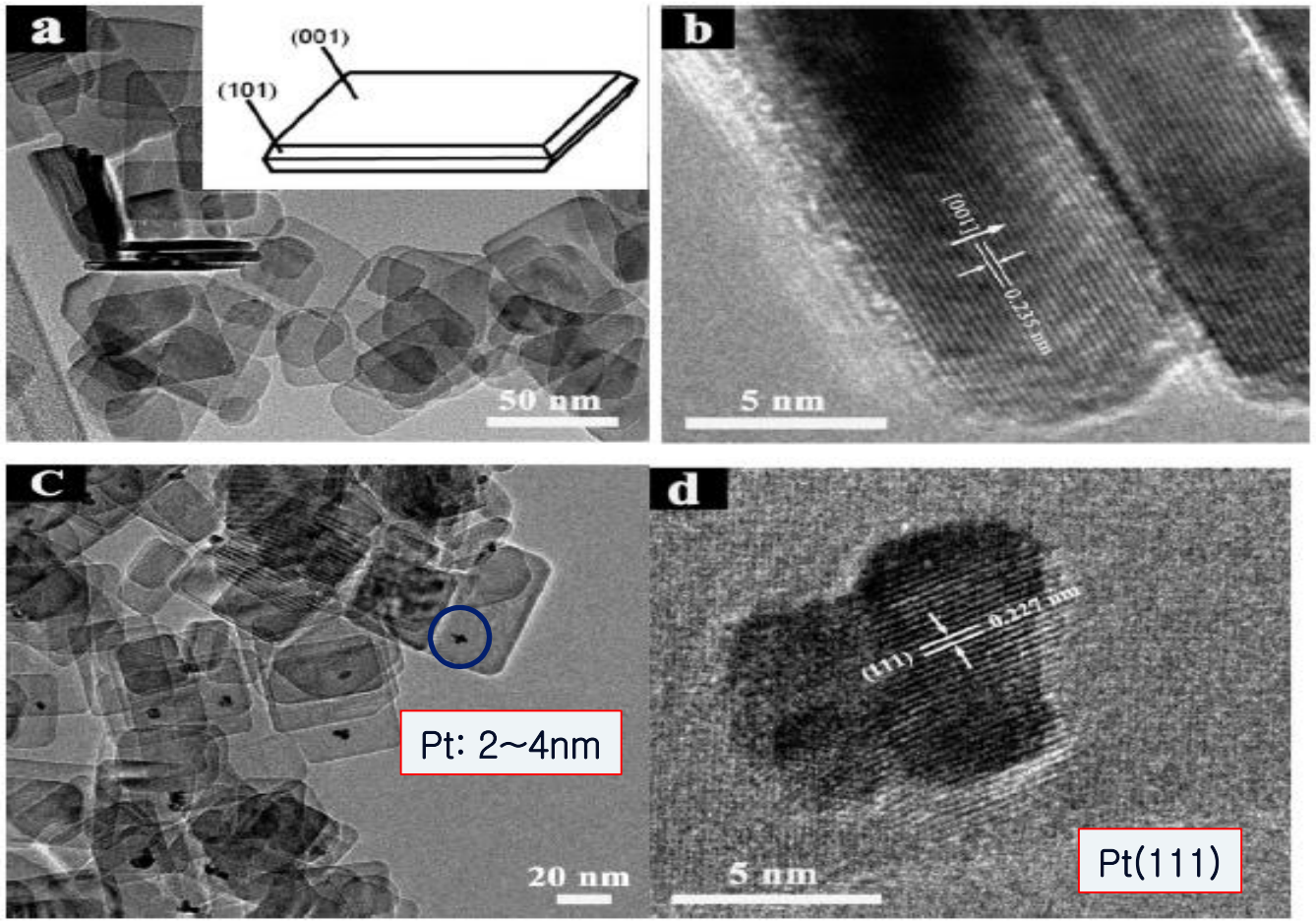


Figure 1. TEM (a and c) and HRTEM (b and d) images of the samples prepared at $R_{Pt} = 0$ (NS1) (a and b) and $R_{Pt} = 2$ (NS4) (c and d).

Exposed (001) facets was 75%

samples	R_{Pt}
NS1	0
NS2	0.5
NS3	1
NS4	2
NS5	4
NS6	6

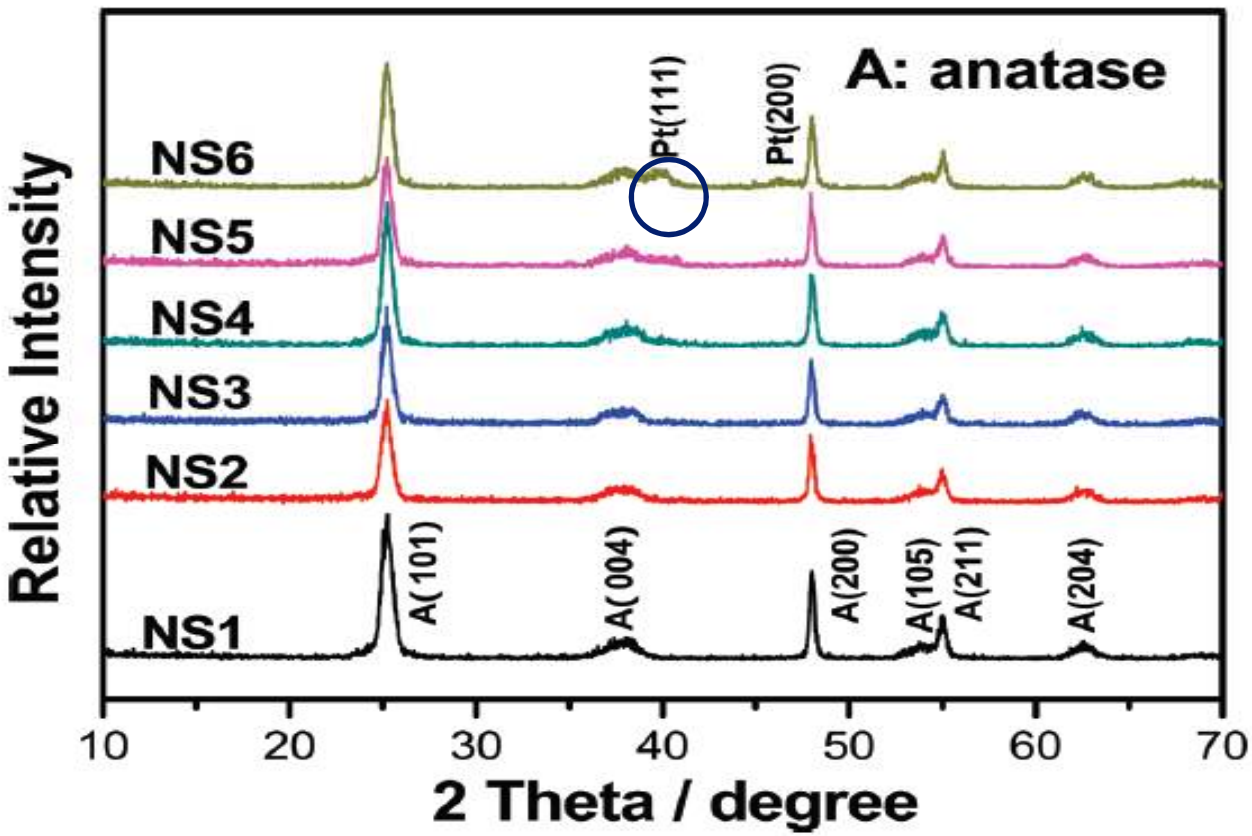


Figure 2. XRD patterns of the samples prepared at $R_{Pt} = 0$ (NS1), 0.5 (NS2), 1 (NS3), 2 (NS4), 4 (NS5), and 6 (NS6).

TABLE 2: Effects of R_{Pt} on the Physical Properties and Photocatalytic Activity of the Samples

samples	R_{Pt}	crystalline size (nm)	S_{BET} (m^2/g)	pore volume (cm^3/g)	average pore size (nm)	activity μmol h^{-1}
NS1	0	14.9	108	0.53	16.0	3.0
NS2	0.5	15.1	101	0.46	14.8	236.6
NS3	1	15.2	96	0.40	14.6	306.5
NS4	2	15.0	94	0.41	14.4	333.5
NS5	4	14.9	93	0.38	13.2	308.7
NS6	6	14.8	84	0.35	13.0	270.9
NS7	2	15.1	104	0.38	12.4	185.0
P25	2	30.1	41	0.40	35.2	223.4
NP	2	12.0	105	0.10	3.6	170.2

Crystalline size (Scherrer's equation) and morphology were not affected by Pt

Pt decreas surface area, pore volume and pore size

Hysteresis Loops indicate large mesopores (15~16nm)

Meso and Macropores, slitlike

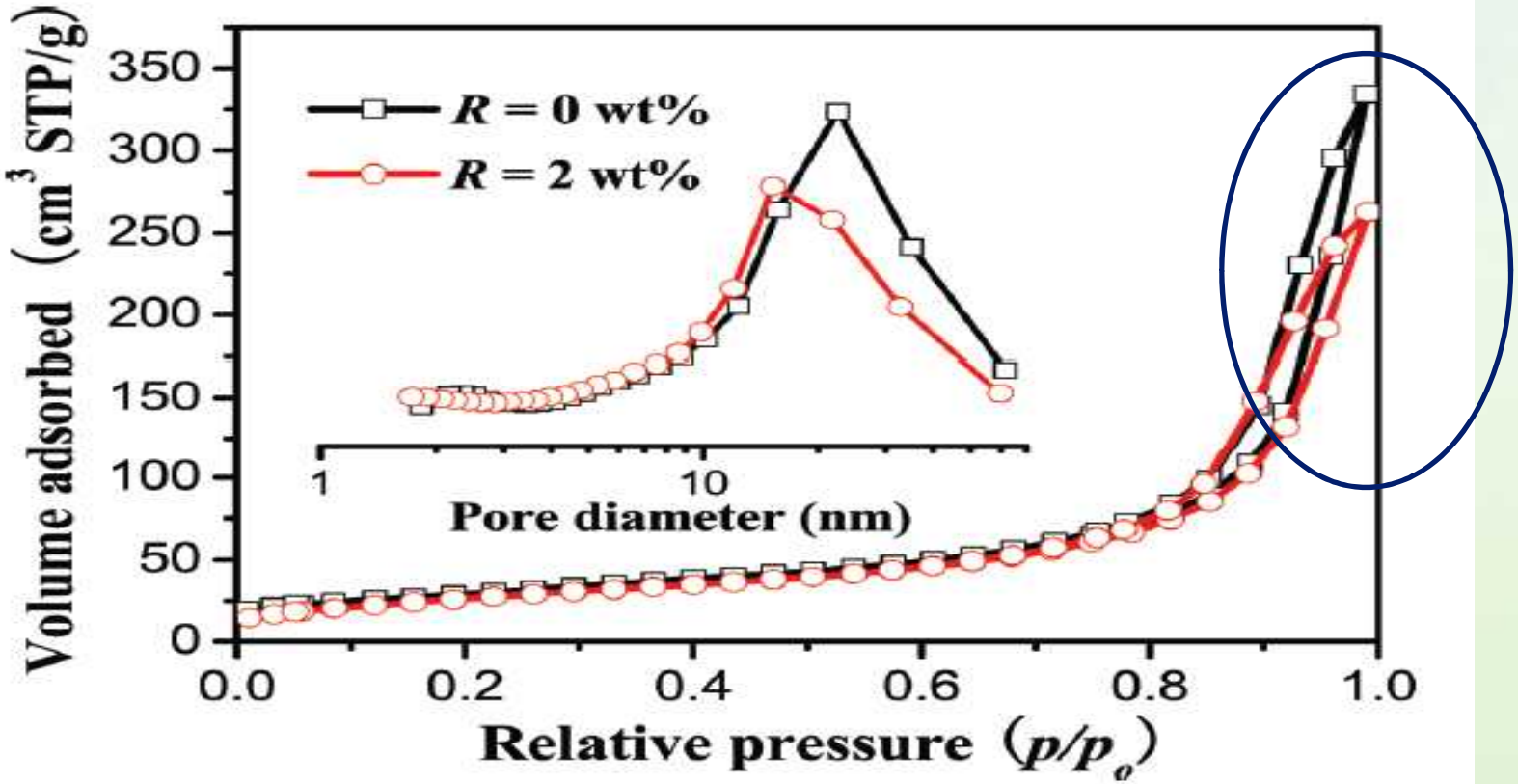
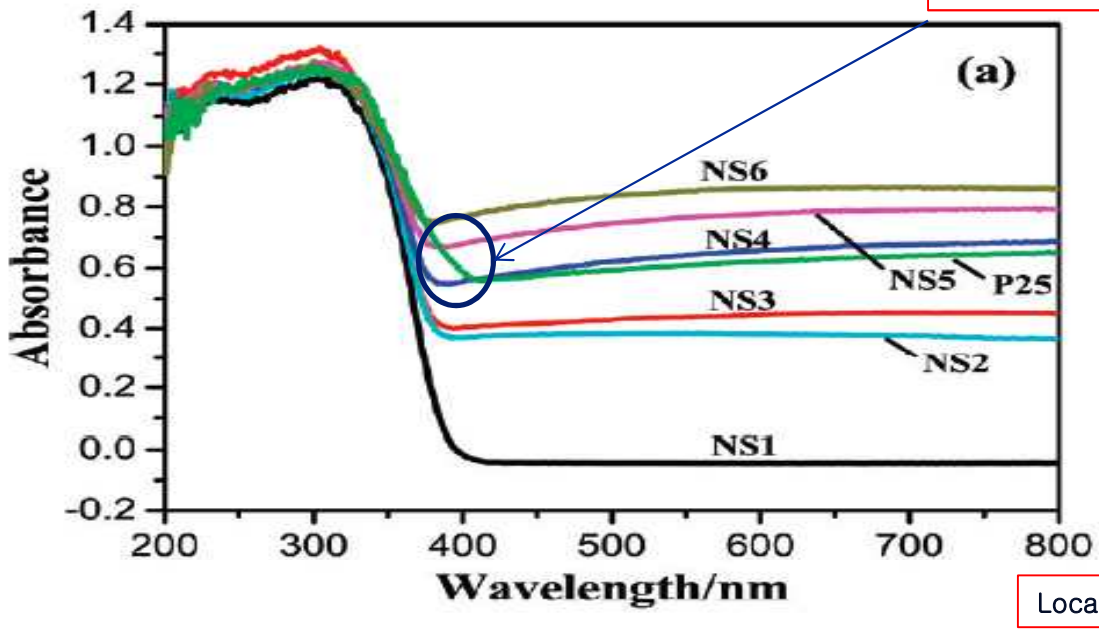


Figure 3. Nitrogen adsorption—desorption isotherms and the corresponding pore-size distribution curves (inset) for the samples prepared at $R_{Pt} = 0$ (NS1) and $R_{Pt} = 2$ (NS4).

Due to aggregation of nanosheets

Rutile of TiO2



Localized Surface Plasmon Resonance

Figure 4. UV−vis absorbance spectra (a) and the corresponding photos (b) of suspensions in water for the samples prepared at $R_{Pt} = 0$ (NS1), 0.5 (NS2), 1 (NS3), 2 (NS4), 4 (NS5), and 6 (NS6) and P25 prepared at $R_{Pt} = 2$ without F.

PL emission results from the recombination of free carriers.
Quenching indicates transferring electron from TiO2 to Pt.

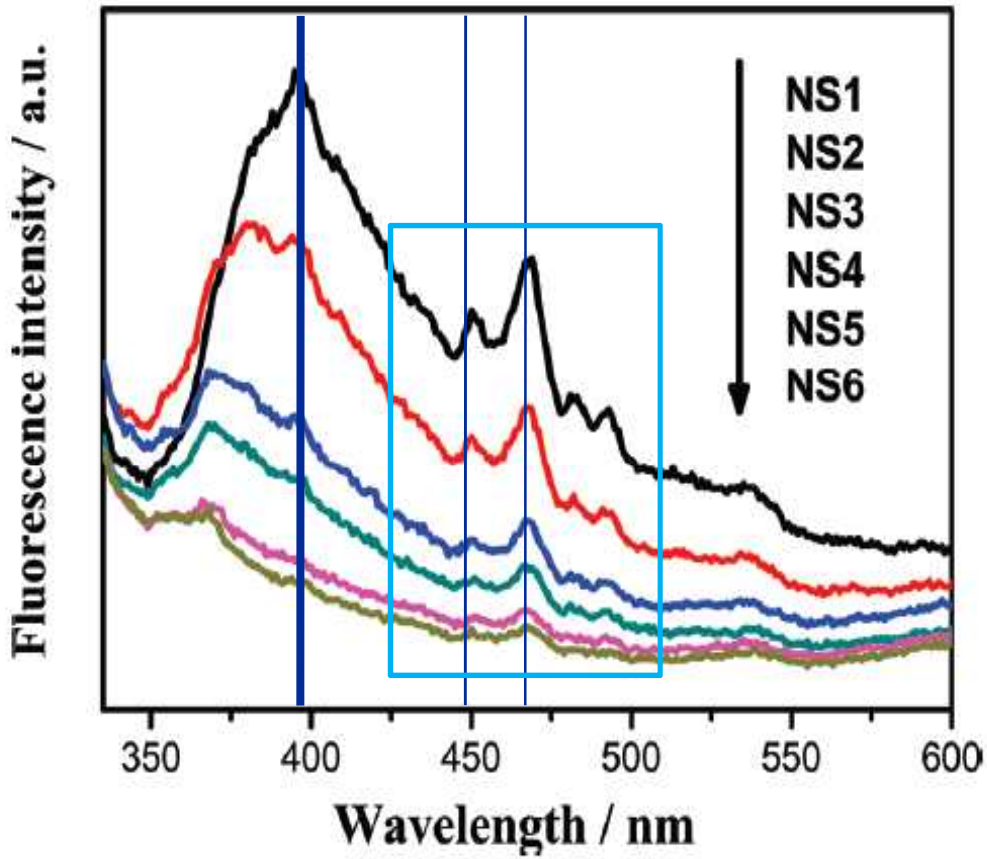
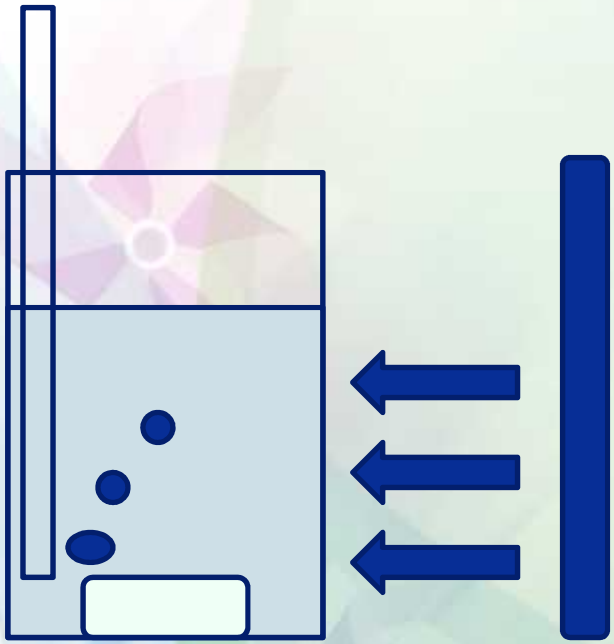


Figure 5. PL spectra of the samples prepared at $R_{Pt} = 0$ (NS1), 0.5 (NS2), 1 (NS3), 2 (NS4), 4 (NS5), and 6 (NS6).

440~500nm: Surface oxygen vacancies and defects of TiO2

Photocatalytic Acctivity



350W Xe Arc Lamp, 20mW/cm^{-2}

0.4ml gas was sampled

H2 was analyzed by GC

20 mg catalyst

EtOH (20ml) + H2O (60ml)

Stirring and N2 was bubbled during reaction

Reduce recombination of electron and hole by Pt

TABLE 2: Effects of R_{Pt} on the Physical Properties and Photocatalytic Activity of the Samples

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Light Scattering and blocking
Decrease of TiO2 Area

F ion plays an important role in photocatalytic reaction.

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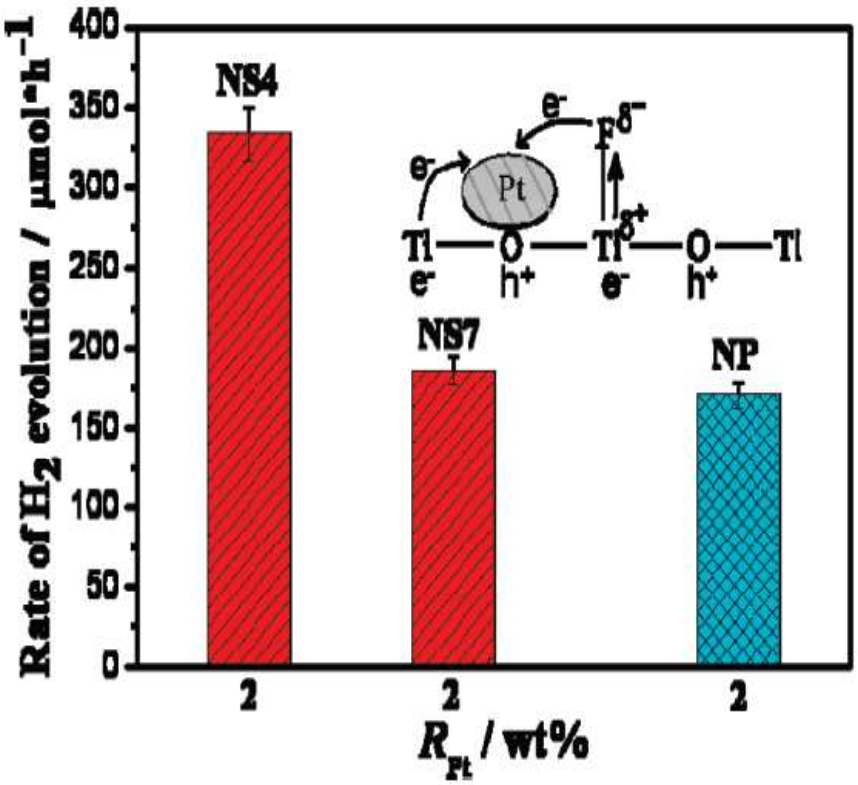
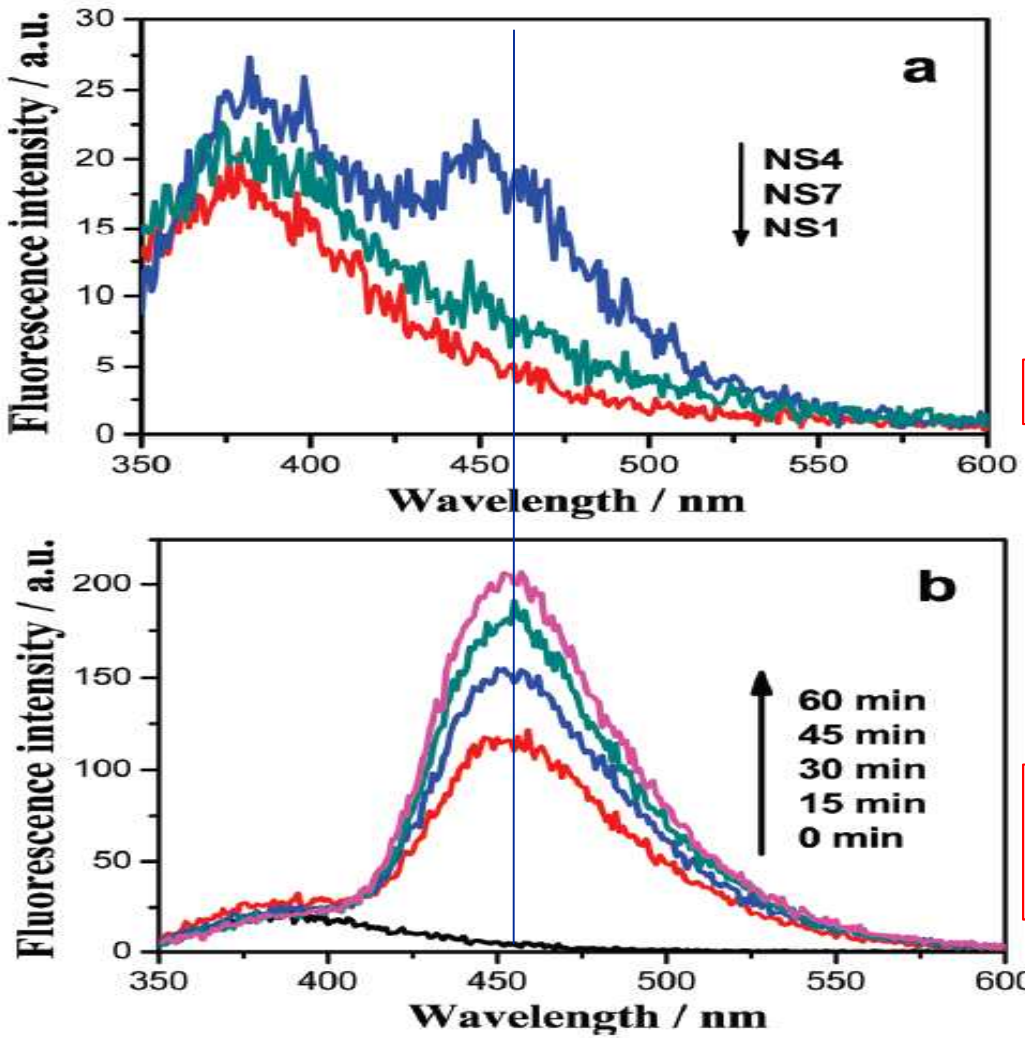


Figure 6. Comparison of the photocatalytic production of H_2 from ethanol aqueous solutions for NS4 (nanosheets with F and $R_{Pt} = 2$), NS7 (nanosheets without F and $R_{Pt} = 2$), and NP (nanoparticles without F and $R_{Pt} = 2$). Inset shows schematic diagram for generation and transfer of photogenerated e^--h^+ pairs in F-TiO_2 under UV irradiation.

F ion is electron-trapping site.

456nm

No PL peak in NS1.
No OH radical produced



Coumarin solution without O2 +UV

Water with O2 +UV:
Electron moves to O2, and
Hole reacts with OH- to make OH

Figure 7. (a) PL spectra of 1×10^{-3} M coumarin ethanol aqueous solutions in an anaerobic environment under UV irradiation for 1 h for the samples prepared at $R_{Pt} = 0$ (NS1), $R_{Pt} = 2$ (NS4), and $R_{Pt} = 2$ without F (NS7); (b) PL spectral changes observed during illumination of NS1 prepared at $R_{Pt} = 0$ in a 1×10^{-3} M coumarin aqueous solution in air and each PL spectrum was recorded every 15 min.

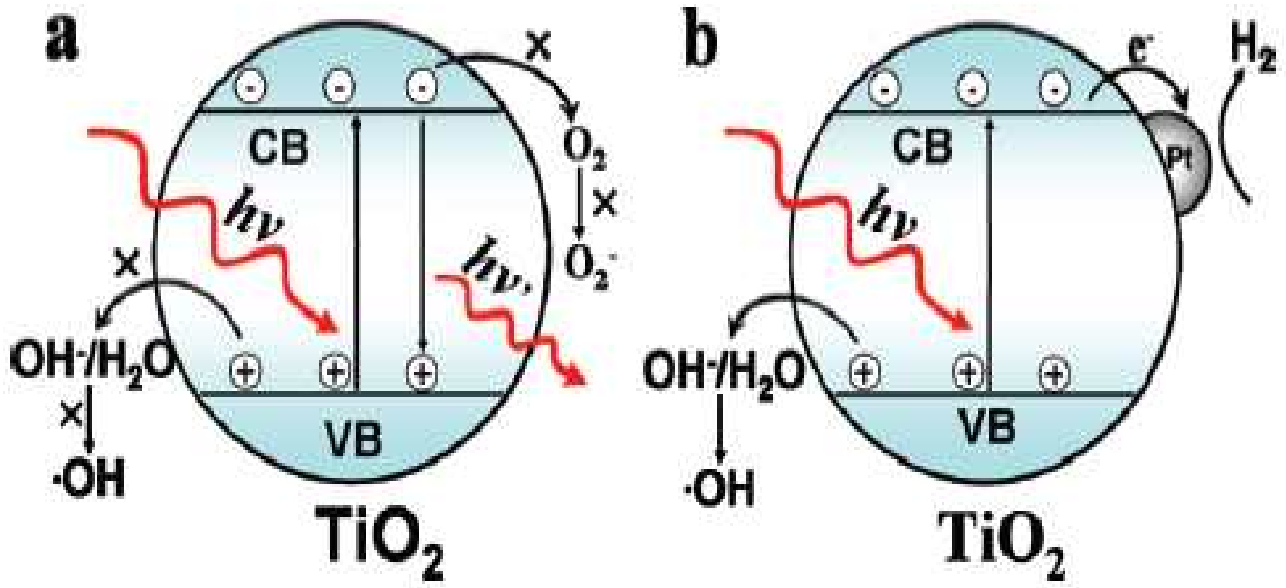


Figure 8. Transfer and separation of photogenerated electrons and holes on the surface of TiO_2 in an anaerobic environment and in the absence (a) and presence (b) of Pt.

PHOTOCATALYSTS

Closing the gap

Photocatalysts such as titanium dioxide that use sunlight to split water and produce hydrogen would be a clean and sustainable solution to many problems, but their efficiency is currently too low to be widely used. Two approaches to engineer the surface properties of titanium dioxide offer hope that its efficiency can be increased.

NATURE CHEMISTRY | VOL 3 | APRIL 2011 | www.nature.com/naturechemistry

After cleaning the TiO_2 rutile (011) surface by argon ion irradiation and annealing the sample in a low pressure of oxygen, Batzill and colleagues found that the surface atoms had re-arranged themselves, forming a beautiful hexagonal pattern (Fig. 1b). Photoemission

A group led by Samuel Mao took a different approach to making TiO_2 a more efficient photocatalyst, which they report in *Science*[5]. They synthesized nanosized TiO_2 and reduced it in a hydrogen atmosphere. The material turned black; certainly a good sign when you want to absorb as much light as possible.

This would close the gap to effectively ~2.1 eV, pushing the optical absorption edge into the visible (590 nm), and achieving the goal of harvesting a larger fraction of the solar

around 1 eV (~1,200 nm).