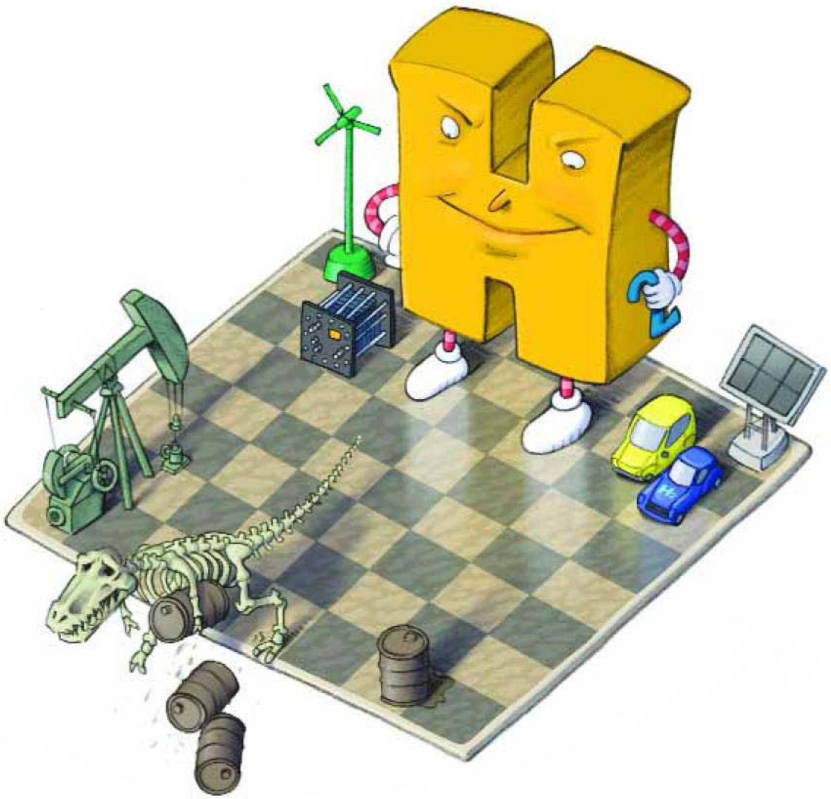
Nanocomposite Photocatalysts for Solar Hydrogen Production



Hydrogen Economy

Carbon Economy

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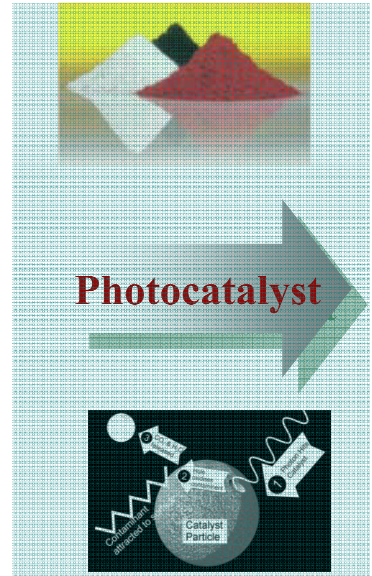
POSTECH
Dept. of Chemical Engineering

ECOCA

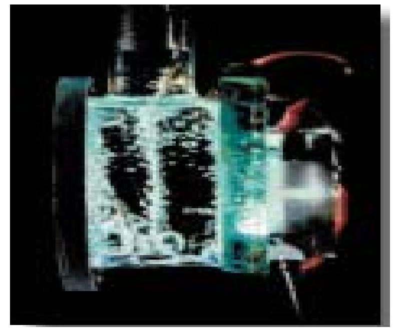
Photocatalytic Hydrogen Production

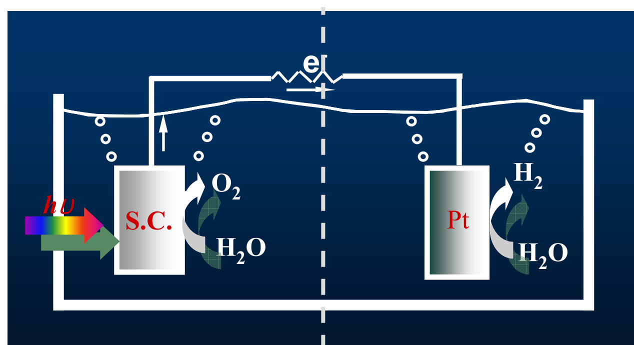


Sunlight for Hydrogen Production

PV /Electrolysis

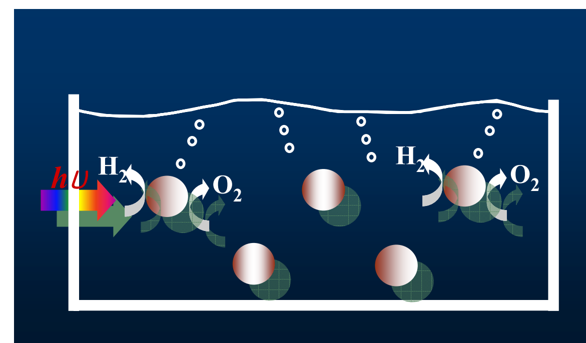
Photoelectrochemical (PEC) Cell





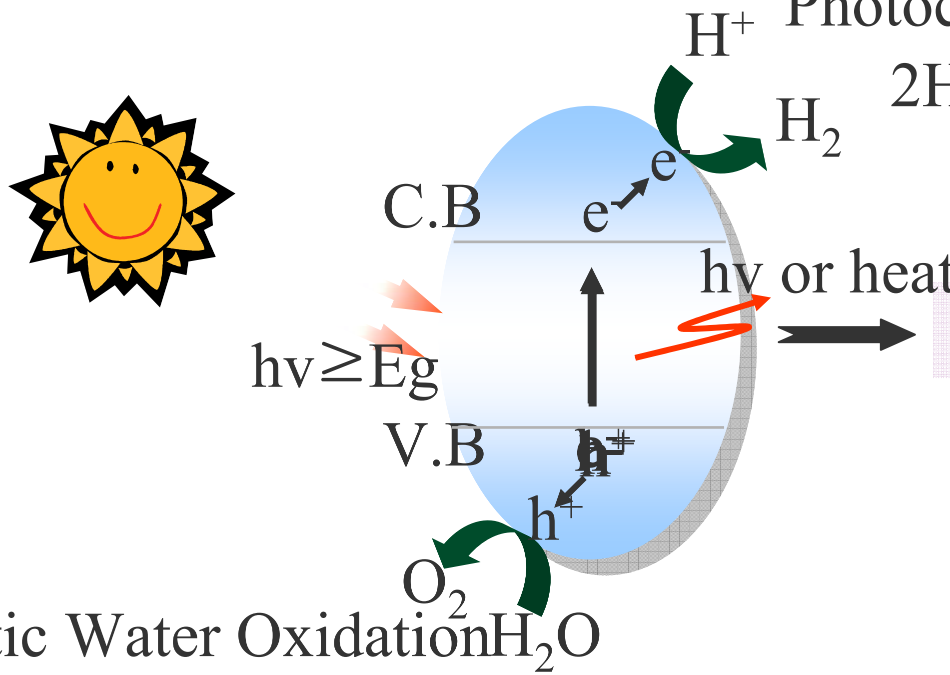
- No need for H_2/O_2 separation
- High efficiency
- Low stability
- Fabrication cost

Photocatalysis



- Low cost
- Low efficiency at present

Photocatalytic Water Splitting by Particulate Photocatalysts



Photocatalytic Water Reduction

$2H^+ + 2e^- \rightarrow H_2$

Recombination !!

Low Quantum Yield

Low Photo-Activity !

Photocatalytic Water Oxidation

$H_2O + 2h^+ \rightarrow \frac{1}{2}O_2 + 2H^+$

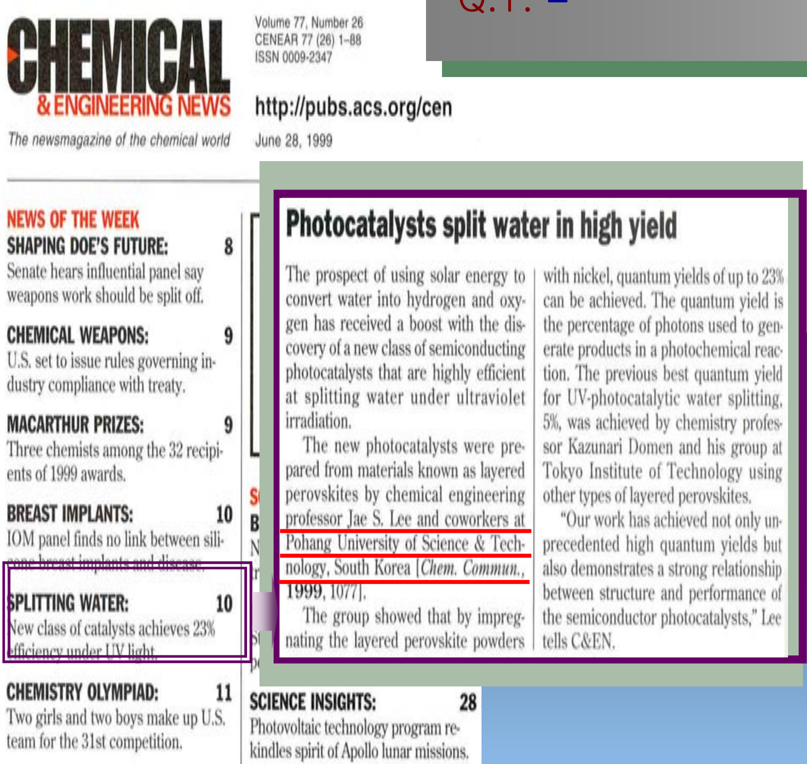
Photocatalytic Overall Water Splitting

$$H_2O + hv \rightarrow H_2 + \frac{1}{2}O_2 \quad (E = -1.23eV)$$

Overall Water Splitting under UV light

$$Q.Y. = \frac{2\times \text{ number of hydrogen molecules (or } 4\times \text{ number of oxygen molecules)}}{\text{Number of photons abosorbed}}$$

H. G. Kim et al., Chem. Comm., 1077-1078 (1999)
D. W. Hwang et al., J. Catal., 193, 40-48 (2000)
J. Kim, Chem. Comm., 2488-2489 (2002)
D. W. Hwang et al., J. Phys. Chem., 109(6), 2093-2102 (2005)



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NEWS OF THE WEEK

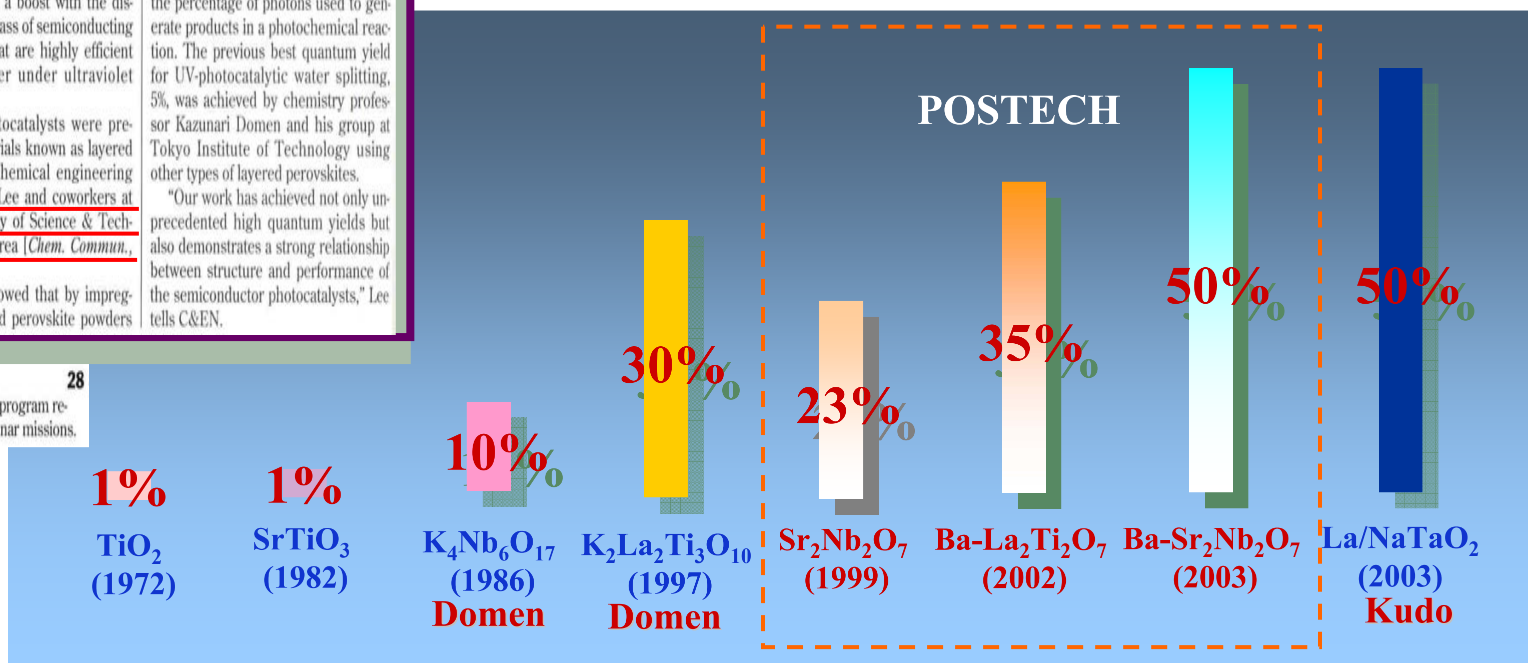
Photocatalysts split water in high yield

The prospect of using solar energy to convert water into hydrogen and oxygen has received a boost with the discovery of a new class of semiconducting photocatalysts that are highly efficient at splitting water under ultraviolet irradiation.

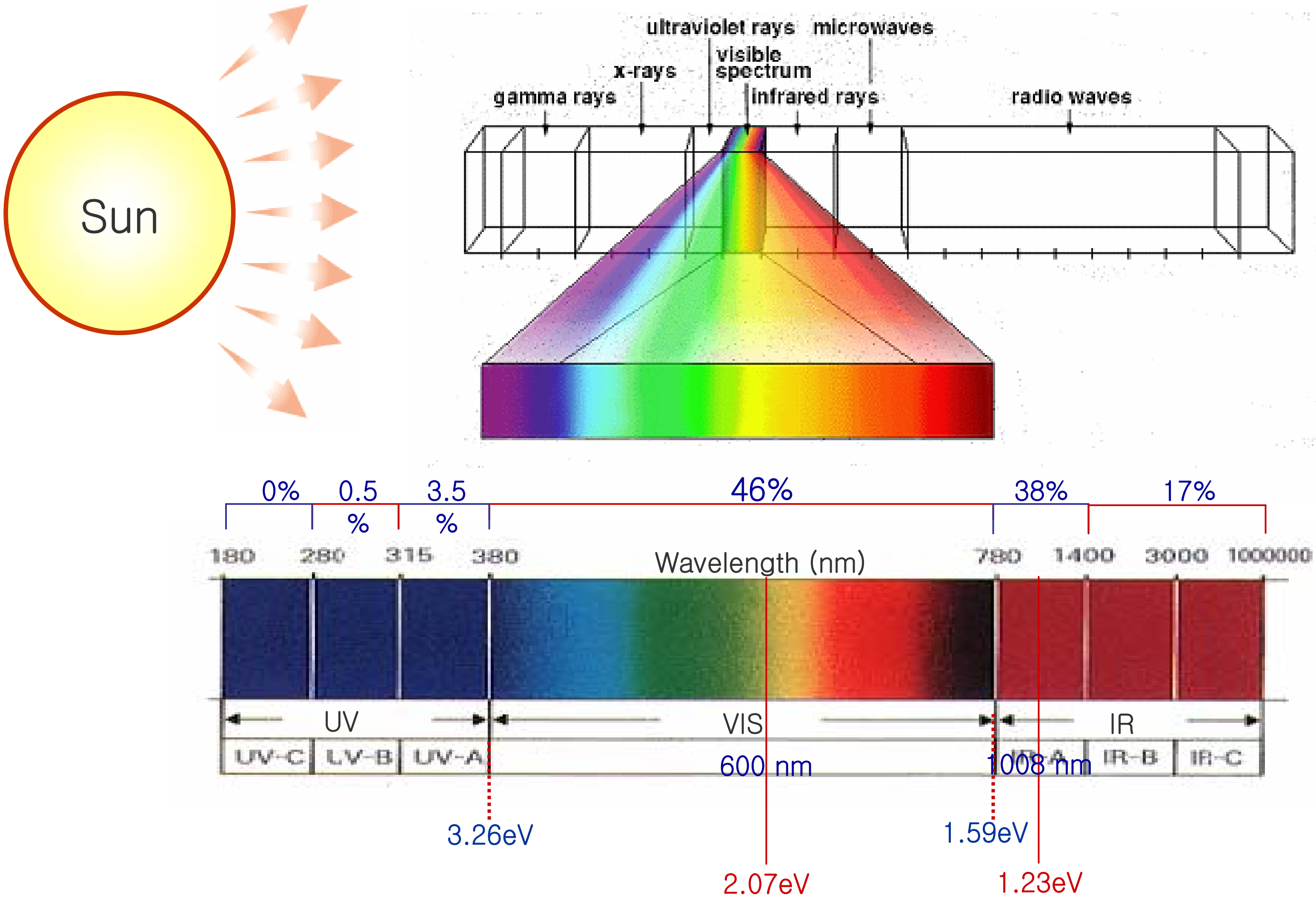
The new photocatalysts were prepared from materials known as layered perovskites by chemical engineering professor Jae S. Lee and coworkers at Pohang University of Science & Technology, South Korea [*Chem. Commun.*, 1999, 1077].

The group showed that by impregnating the layered perovskite powders with nickel, quantum yields of up to 23% can be achieved. The quantum yield is the percentage of photons used to generate products in a photochemical reaction. The previous best quantum yield for UV-photocatalytic water splitting, 5%, was achieved by chemistry professor Kazunari Domen and his group at Tokyo Institute of Technology using other types of layered perovskites.

"Our work has achieved not only unprecedented high quantum yields but also demonstrates a strong relationship between structure and performance of the semiconductor photocatalysts," Lee tells C&EN.



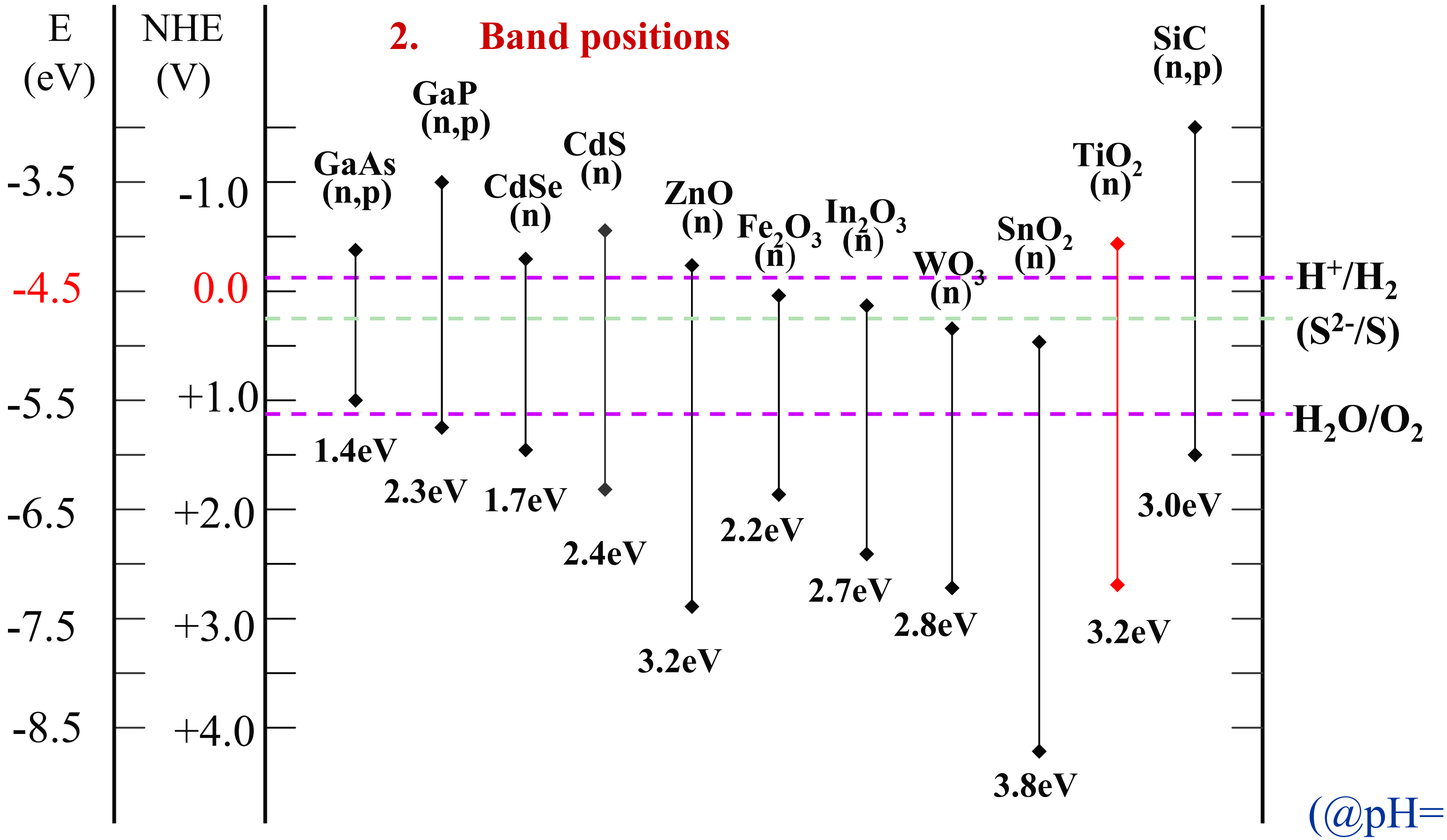
Solar Light Spectrum



Band Gaps and Band Positions

Two Requirements for Band Structure:

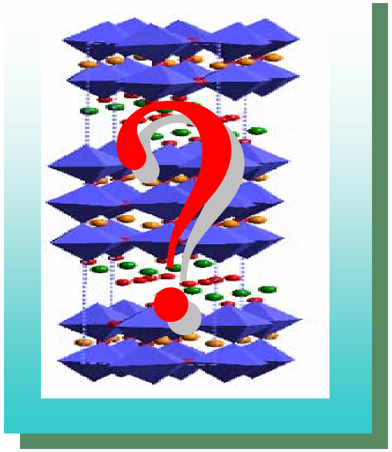
1. **Band gap: 1.6 eV < Eg < 3.0eV**
2. **Band positions**



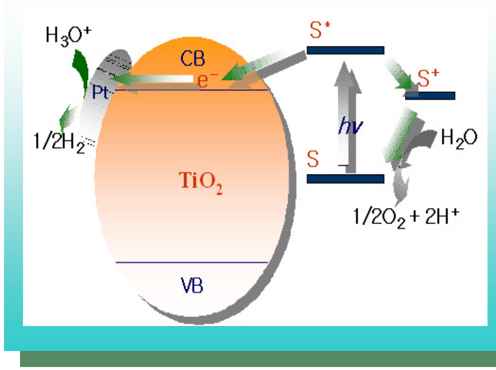
Search for the Visible Light Photocatalysts

1. New Single Phase Materials
2. Photosensitizer (PS)
3. Modification of UV Photocatalysts
   - Cation Doping
   - Anion Doping (Nitrides, Carbides, Sulfides)
4. Composite Photocatalysts
5. Solid Solution

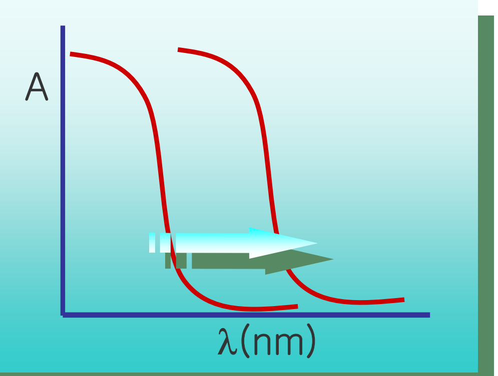
1. New Single Phase Materials



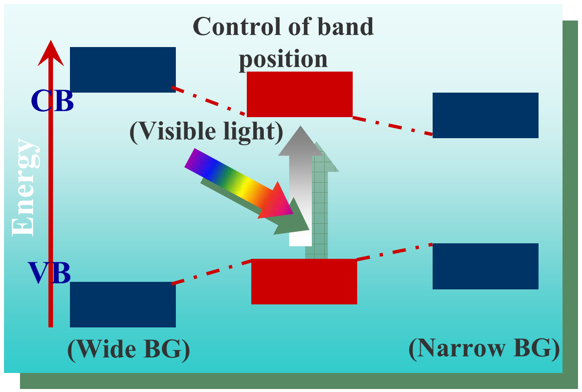
2. Photosensitizer (PS)



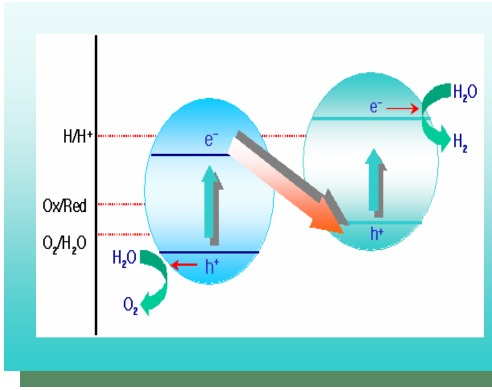
3. Modification



5. Solid Solution

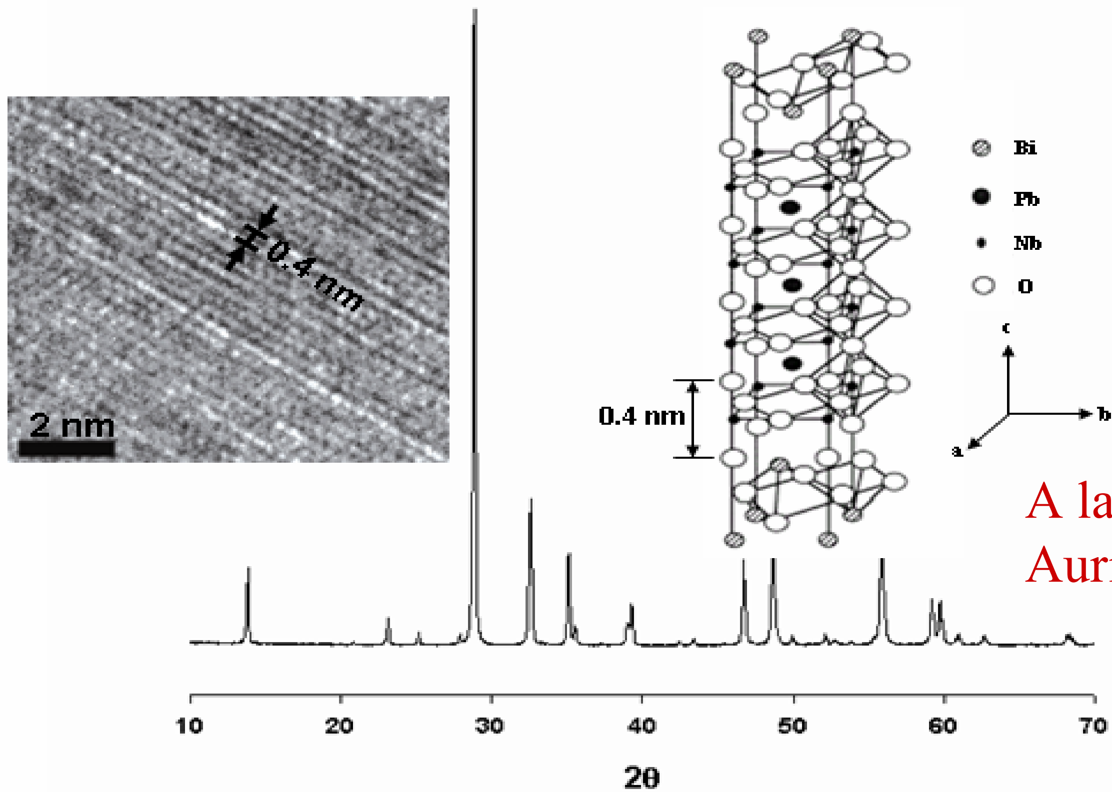


4. Composite Photocatalysts



A Novel Undoped, Single phase, Photocatalyst, $PbBi_2Nb_2O_9$

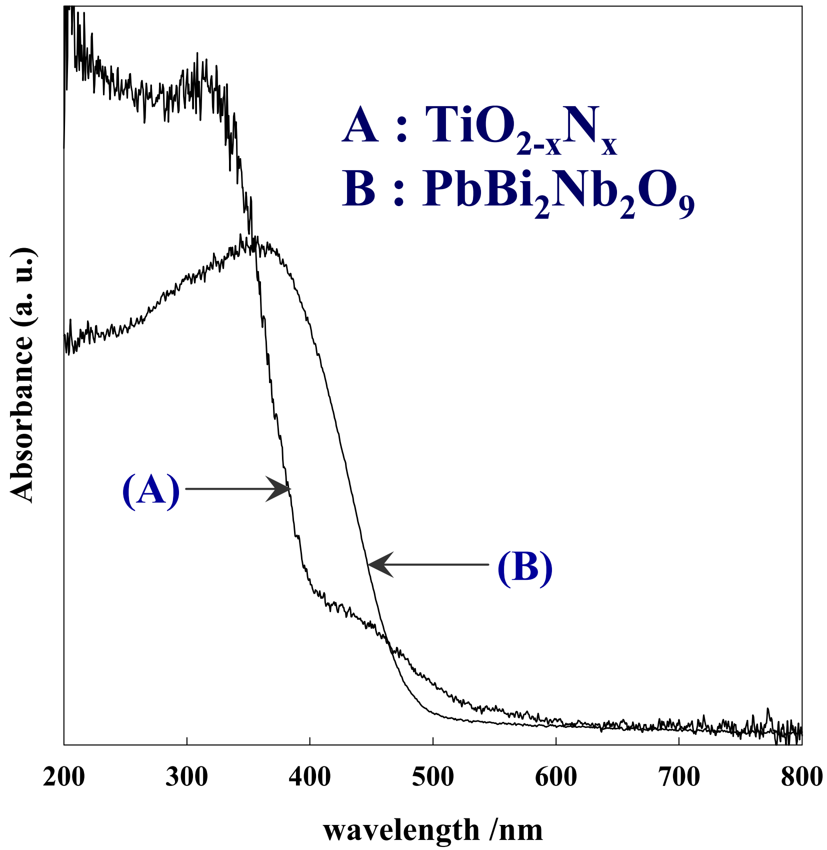
J. Am. Chem. Soc., 126(29), 8912-8913 (2004
J. Solid State Chem., 179, 1211-1215 (2006)



A layered perovskite of Aurivillius phase

X-ray diffraction pattern and the high-resolution TEM image of $PbBi_2Nb_2O_9$ sintered at 1473K for 24h and its structure model

Optical Properties



(A)

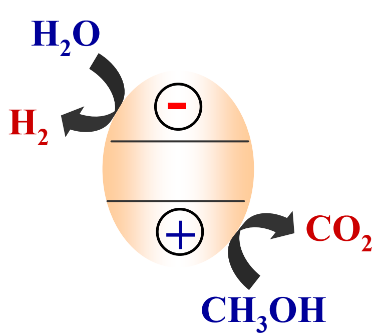
(B)

UV-Vis Diffuse Reflectance spectra

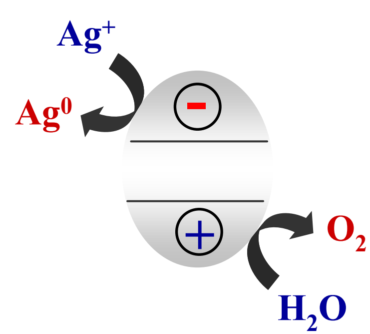
Water Splitting with Sacrificial Agents (λ≥420 nm)

Catalysts	Band Gap Energy		Hydrogen Evolution		Oxygen Evolution	
	E_g(eV)	λ_{ab}(nm)	μmol/gcat•hr	^{3}Q.Y.(%)	μmol/gcat•hr	^{3}Q.Y.(%)
$PbBi_2Nb_2O_9$	2.88	431	7.6	0.95	520	29
$TiO_{2-x}N_y$	2.77	451	trace	0	221	14

- **Catalyst loaded with 1wt% Pt, 0.3g; light source, 450W W-Arc lamp(Oriel) with UV cut-off filter(λ≥420nm). Reaction was performed in aqueous methanol solution (methanol 30ml + distilled water 170ml) or in an aqueous $AgNO_3$ solution(0.05mol/l, 200ml)**

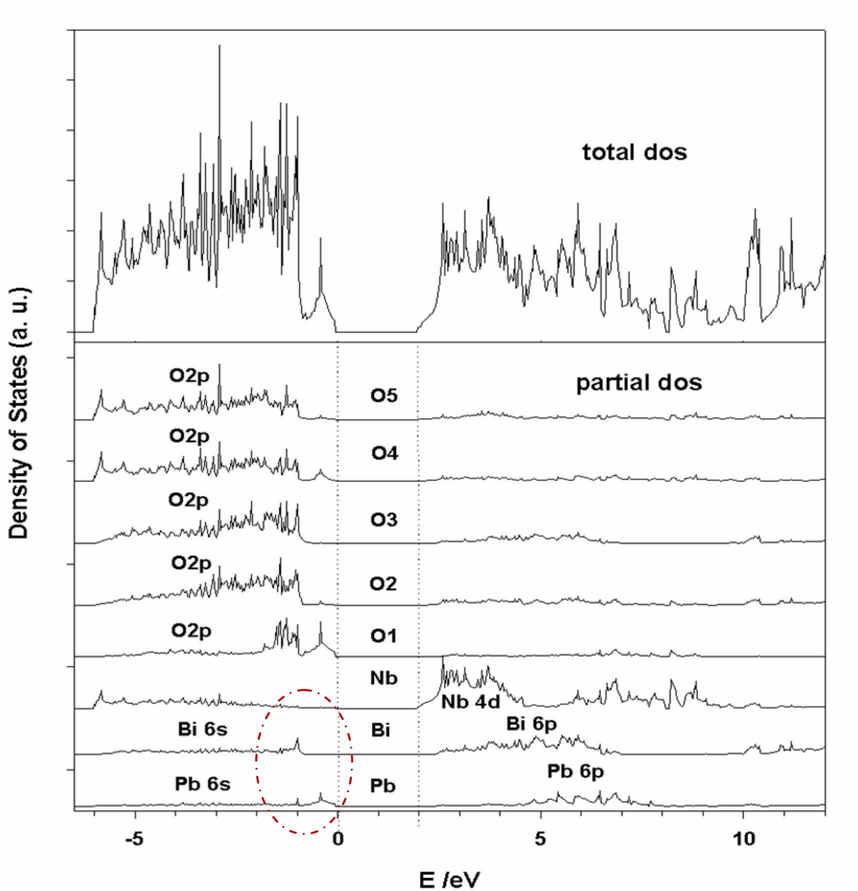


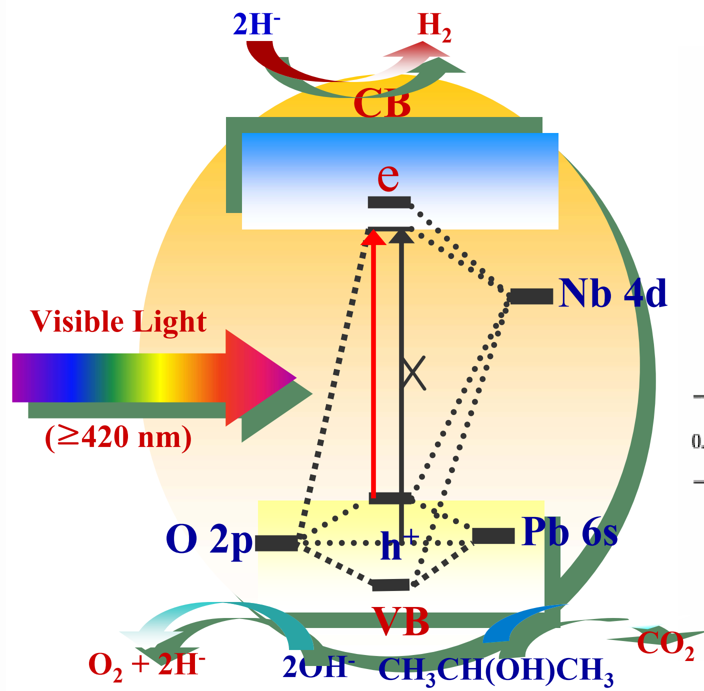
H_2 Evolution



O_2 Evolution

Band Gap Reduction of Layered Perovskites By Pb & Bi





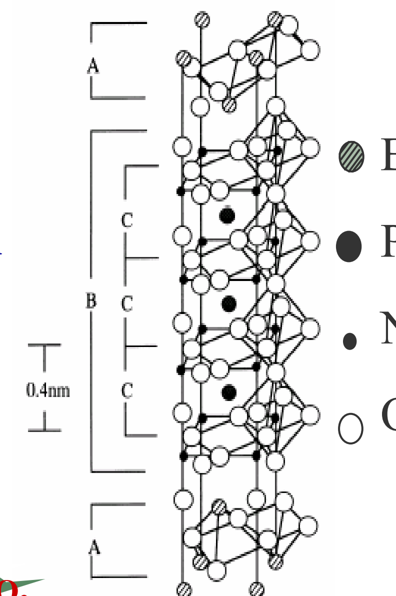
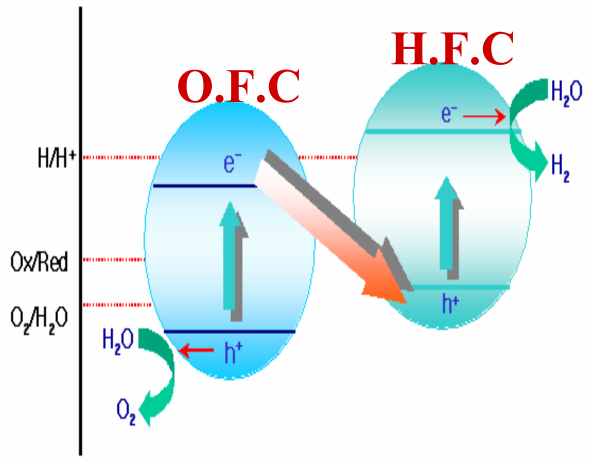
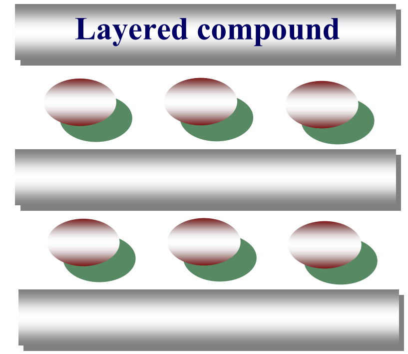


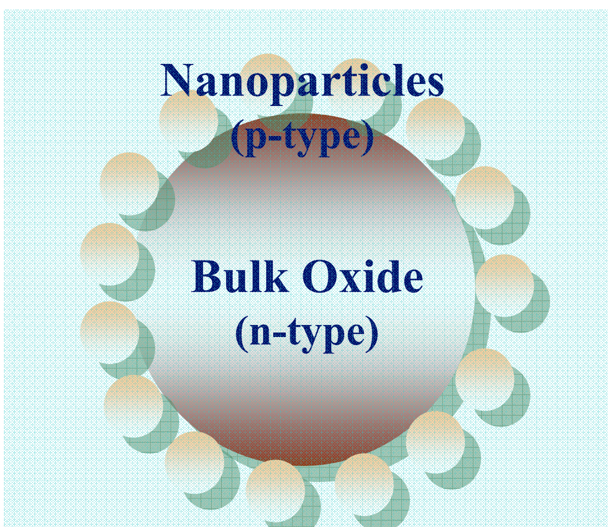
Fig. Total and partial density of states (DOS) of $PbBi_2Nb_2O_9$

Strategies for Development of Composite Photocatalysts





J. S. Jang et. al., J. Catal., 231 (2005) 213

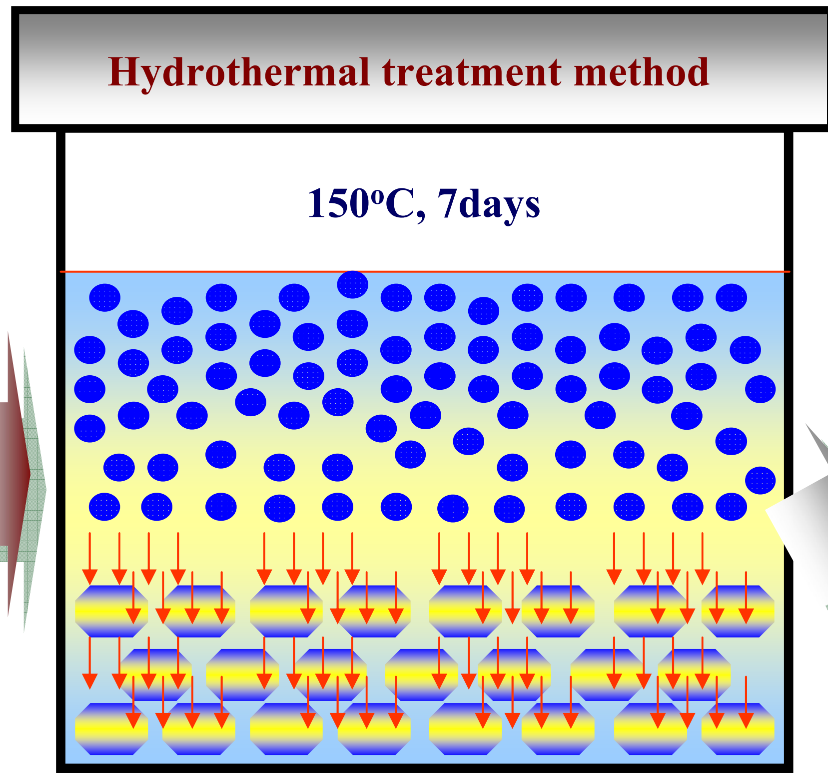


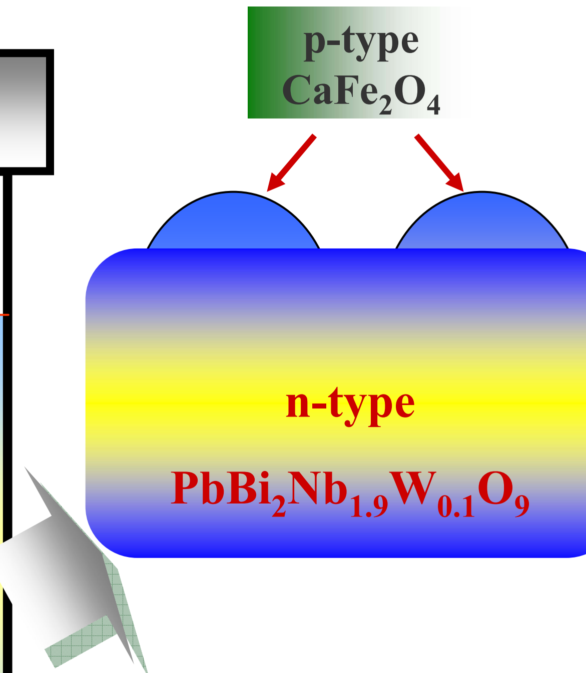
- **What functions ?**
  → **Photocatalytic p-n Nanodiodes (PCD)**
- **How to fabricate ?**
  → **Nano-Bulk Composite (NBC)**

Photocatalytic p-n Nanodidoes

: $CaFe_2O_4$

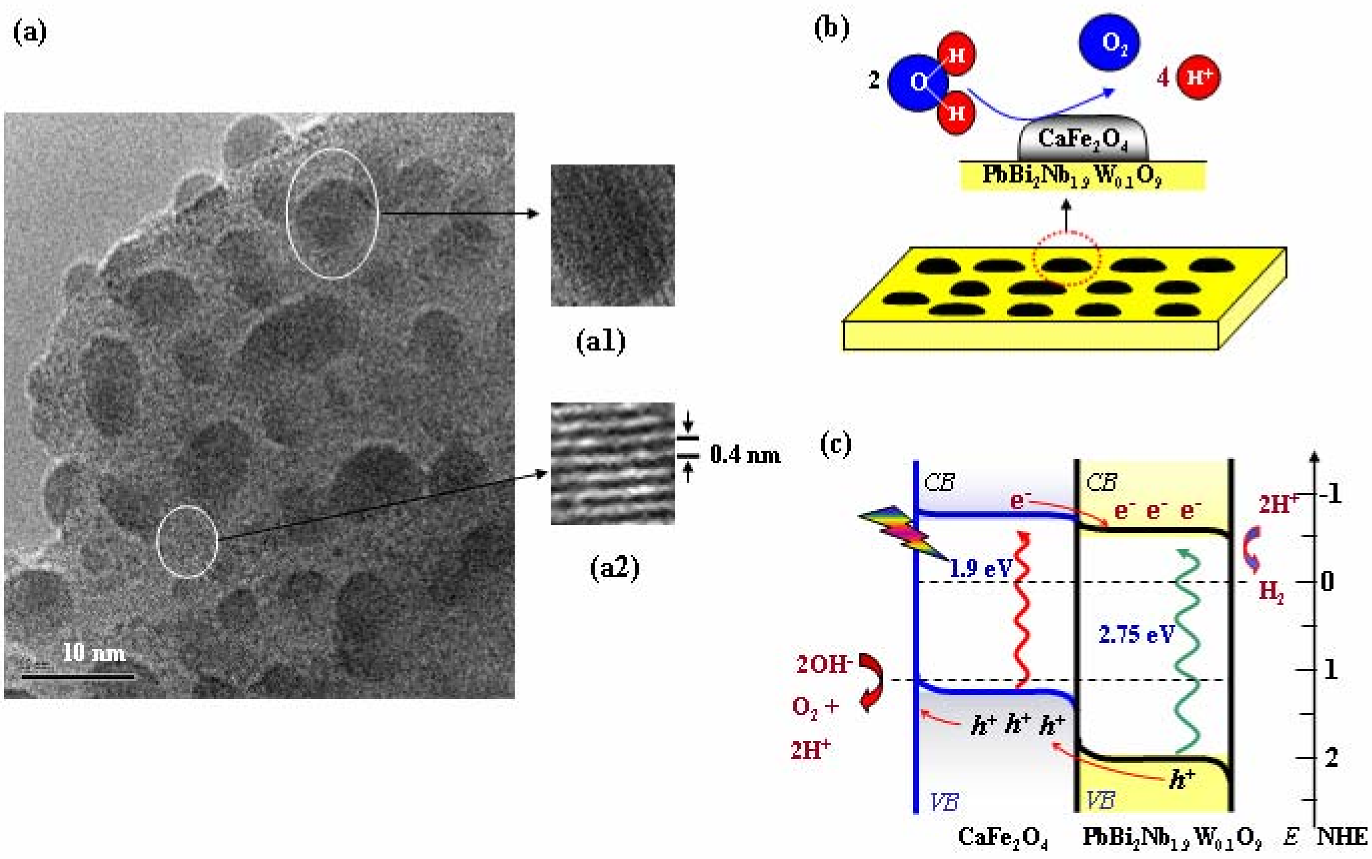
: $PbBi_2Nb_{1.9}W_{0.1}O_9$





- $PbBi_2Nb_{1.9}W_{0.1}O_9$ synthesized by the solid state reaction method.
- $CaFe_2O_4$ synthesized by the sol-gel method.

Photocatalytic p-n Nanodiodes (PCD)



Angew. Chem. Int. Ed. 44 (2005) 4585

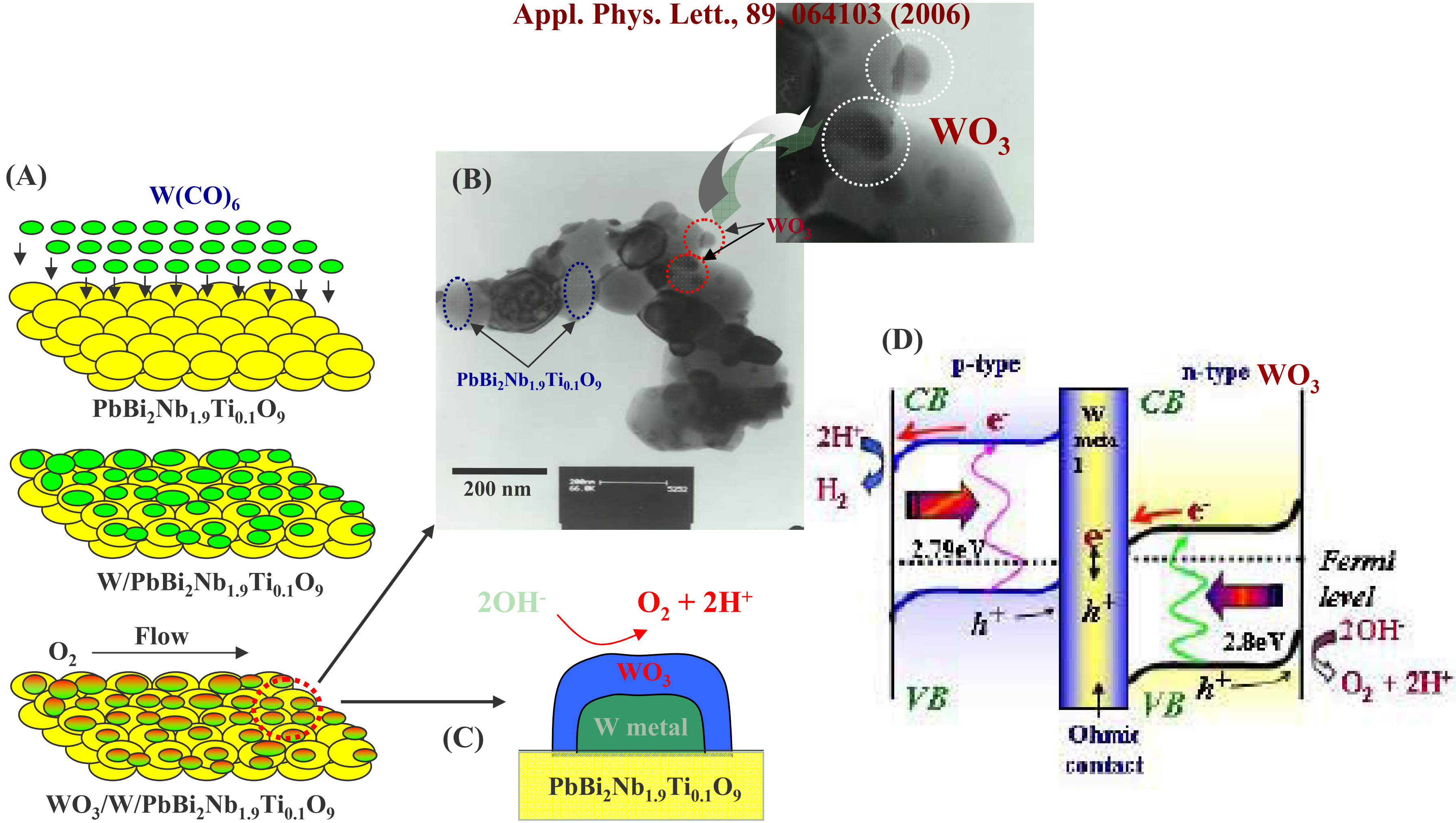
Water Splitting with Sacrificial agents ($\lambda \geq 420$ nm)

Catalysts	Band Gap Energy		Hydrogen Evolution		Oxygen Evolution	
	E_g(eV)	λ_{ab}(nm)	μmol/gcat•hr	^{3}Q.Y.(%)	μmol/gcat•hr	^{3}Q.Y.(%)
$CaFe_2O_4$/ $PbBi_2Nb_{1.9}W_{0.1}O_9$	2.75	450	34.8	4.16	675	38
$PbBi_2Nb_2O_9$	2.88	431	7.6	0.95	520	29
$CaFe_2O_4$	1.99	623	trace	0	trace	0
$TiO_{2-x}N_y$	2.77	451	trace	0	221	14

Catalyst loaded with 0.1wt% Pt, 0.3g; light source, 450W W-Arc lamp(Oriel) with UV cut-off filter($\lambda \geq 420$nm). Reaction was performed in aqueous methanol solution (methanol 30ml + distilled water 170ml) or in an aqueous $AgNO_3$ solution(0.05mol/l, 200ml).

Photocatalytic p-n Nanodiodes with an Ohmic Junction

Appl. Phys. Lett., 89, 064103 (2006)



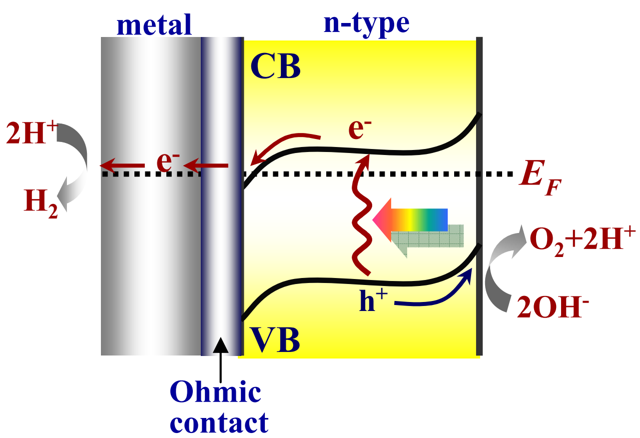
Photocatalytic H_2 and O_2 evolution from water under visible light ($\lambda \geq 420$nm)

Catalysts	Band Gap Energy		Hydrogen Evolution		Oxygen Evolution	
	E_g(eV)	λ_{ab}(nm)	μmol/gcat•hr	[3]Q.Y.(%)	μmol/gcat•hr	[3]Q.Y.(%)
$WO_3/W/PbBi_2Nb_{1.9}Ti_{0.1}O_9$	*2.86*	*433*	*49.33*	*6.06*	*741*	*41*
$CaFe_2O_4/PbBi_2Nb_{1.9}W_{0.1}O_9$	2.75	450	34.8	4.16	675	38
$PbBi_2Nb_2O_9$	2.88	431	7.6	0.95	520	29
$CaFe_2O_4$	1.99	623	trace	0	trace	0
$TiO_{2-x}N_y$	2.77	451	trace	0	221	14

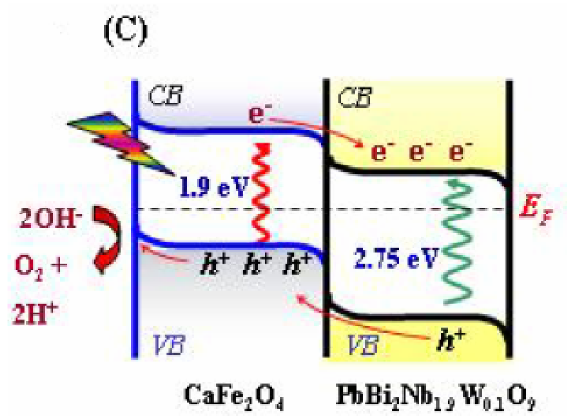
Catalyst loaded with 0.1wt% Pt, 0.3g; light source, 450W W-Arc lamp(Oriel) with UV cut-off filter($\lambda \geq 420$nm). Reaction was performed in aqueous methanol solution (methanol 30ml + distilled water 170ml) or in an aqueous $AgNO_3$ solution(0.05mol/l, 200ml).

p-n Nanocomposite Photocatalysts - Summary

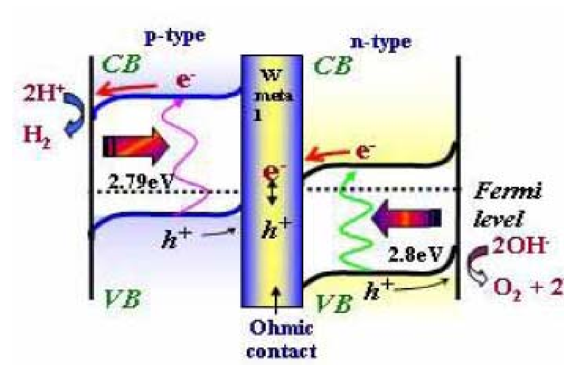
Schottky



p-n



p-n/ohmic



chottky
unction

- One photon process
- Effective h^+-e^- separation

- One photon process
- Effective h^+-e^- separation

- Two photon process
- Higher net photonenergies while absorbing long wavelength photon
- Effective h^+-e^- separation

Ecocat People

$$ponsor

- General Motors
- National Research Laboratory

Hydrogen Energy R&
Center (The 21st Centu
Frontier R&D Program)

Ecoca