Solar Fuels and Environmental Remediation Using Inorganic Semiconductor-Aqueous Solution Interfaces: The Path Traveled and the Way Forward

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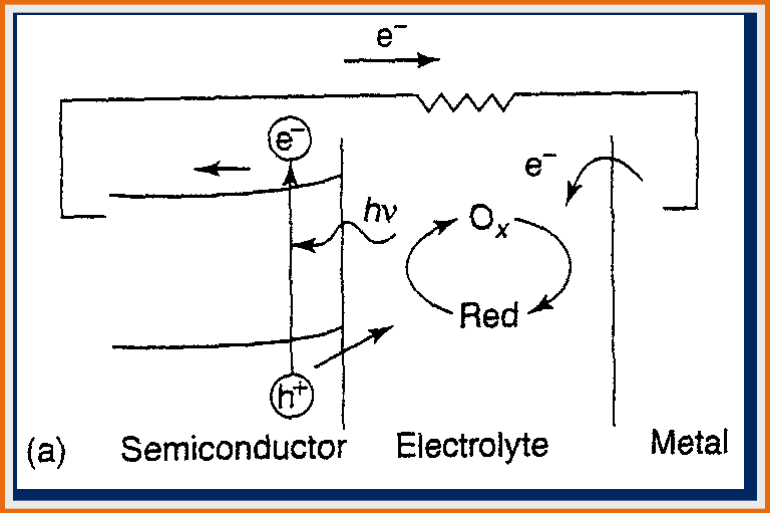
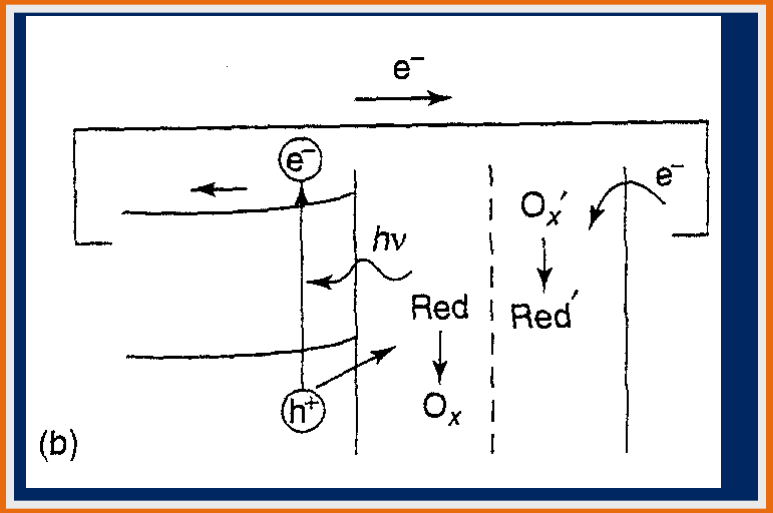
Types of Photoelectrochemical Devices





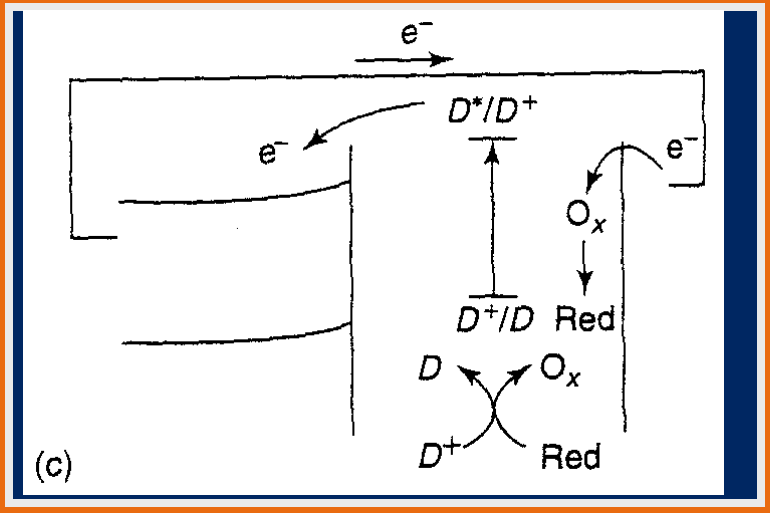


Fig. 27 Types of photoelectrochemical devices for solar energy conversion. (a), (b), and (c) depict regenerative, photoelectrolytic, and dye-sensitized configurations, respectively. As in the remainder of this chapter, an *n*-type semiconductor is assumed in these cases for specificity.

Talk Outline

- The Wheel Has Been Around!
- Historical Evolution of Photoelectrochemistry and Solar Water Splitting
- Photocatalyst Materials
- Mild Synthesis of Inorganic Semiconductors
- Value-Added Approaches

The Wheel Has Been Around!

Photovoltaic Effect

Becquerel - 1839
Solar cell -1954

3G PV Concepts

MEG – Auger effect: Auger, Meitner 1922
Avalanche photodiodes

Dye Sensitization

Hauffe – 1960s
Matsumura – 1970s
Tributsch – 1970s

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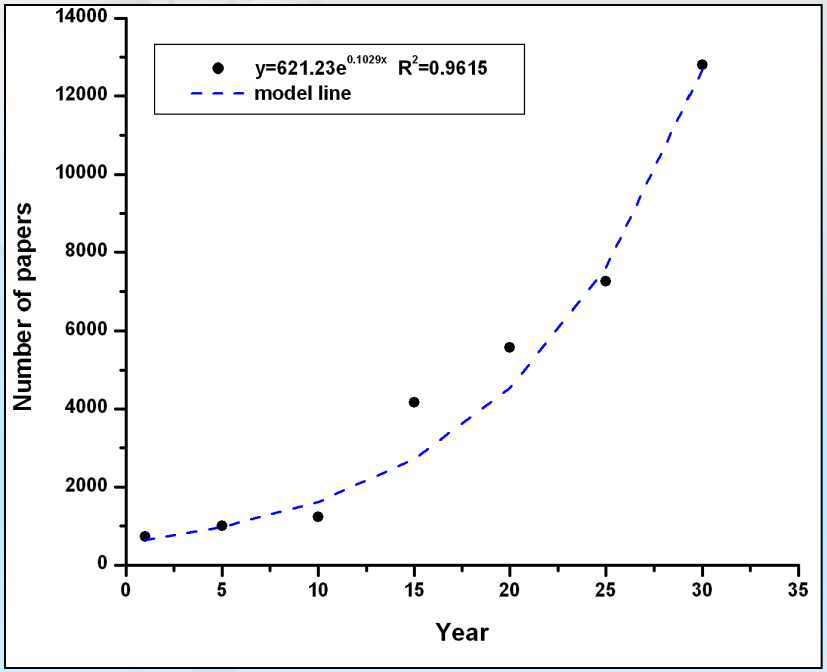
Photoelectrochemical Solar Cells:History

- **Early Years: 1950s-1975**
- **Boom Period: 1975-1982**
- **Deep Funk: 1982-1989**
- **Déjà Vu All Over Again: 1990-present**

K. Rajeshwar, *J. Phys. Chem. Lett.* (Guest Commentary) 2011, *2*, 1301-1309.

Generation	Representative Names
1G	Heinz Gerischer, Allen Bard, Rudi Memming, Mark Wrighton, Adam Heller, Barry Miller, Joost Manassen, John Albery, John Goodenough, Roy Morrison, Mike Butler, Art Nozik, Arnim Henglein, Kenichi Honda, Hiroshi Tsubomura, Hideo Tamura, Walter Gomes, Pedro Salvador, Gabor Somorjai, Yuri Pleskov, Helmut Tributsch, Akira Fujishima, Mary Archer
2G	Michael Grätzel, David Ginley, Art Ellis, Nate Lewis, Bruce Parkinson, Carl Koval, Andrew Bocarsly, Prashant Kamat, Reshev Tenne, Andrew Hamnett, Gary Hodes, Laurie Peter, David Cahen, Krishnan Rajeshwar, Norma de Tacconi, Achim Lewerenz, Joseph Hupp, Tom Mallouk, Shozo Yanagida, Yoshihiro Nakato, Daniel Lincot, Claude-Levy Clement, Anders Hagfeldt, Jan Augustynski, Gerald Meyer, John Kelly, Kazunari Domen, John Turner, Kohei Uosaki, Hiroshi Yoneyama, Michio Matsumura
3G	Lou Brus, Paul Alivisatos, Moungi Bawendi, Patrik Schmuki, Craig Grimes, Juan Bisquert, Kyoung-Shin Choi, Daniel Nocera, Charles Lieber, Daniel Vanmaekelbergh, Gerko Oskam, Akihiko Kudo, Paul Maggard, Frank Osterloh, Gerrit Boschloo, Stuart Licht, Song Jin, Peidong Yang, Tsukasa Torimoto, Susumu Kuwabata, Harry Atwater



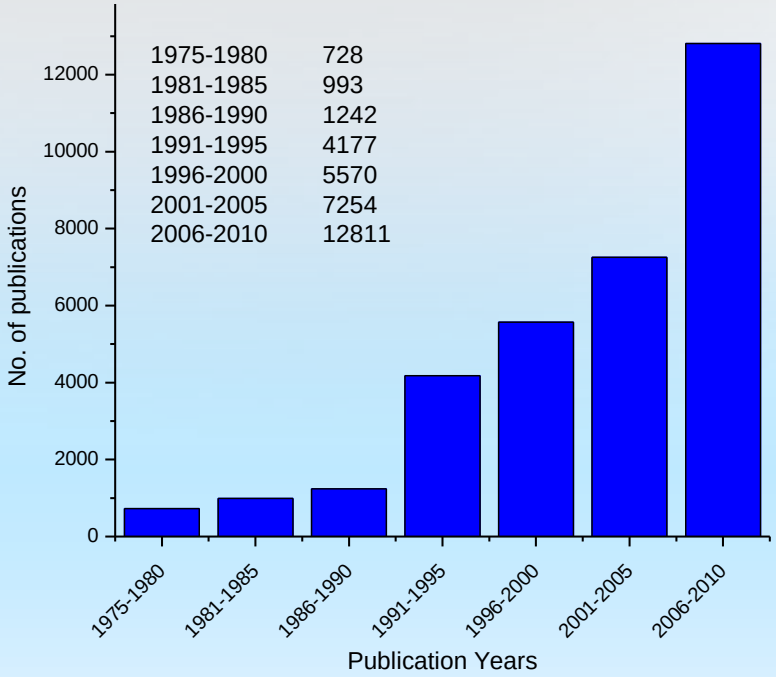
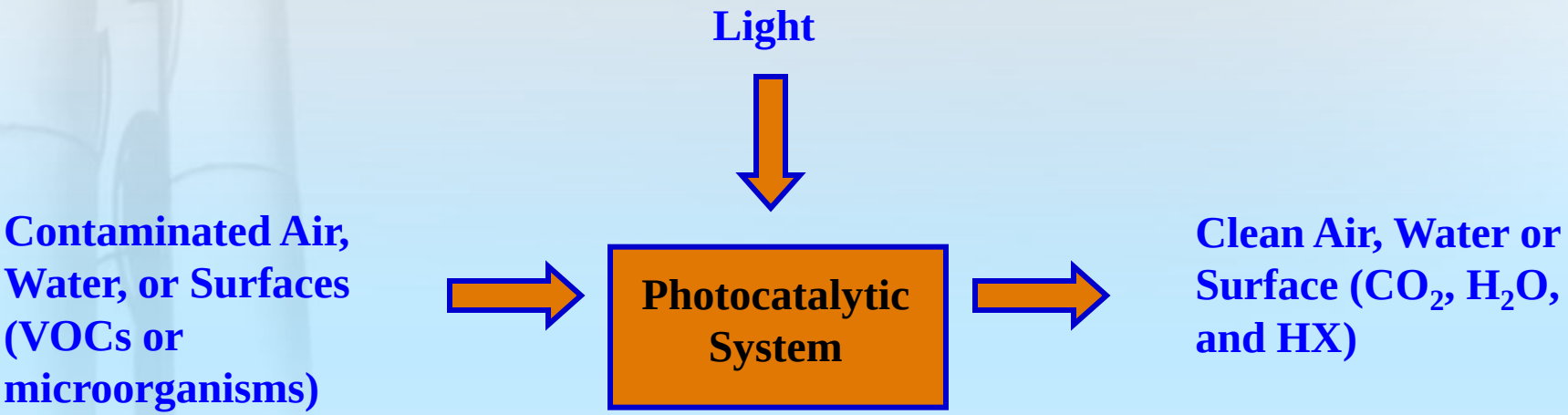


Figure 1. The results from a literature search using the ISI Web of Knowledge database using the keywords: "photoelectrochemistry," "electrochemistry and solar energy conversion," "semiconductor quantum dots and solar energy conversion," and "solar water splitting." The insert contains an exponential fit of the literature search results .

The Photocatalytic Fluid Purification-Process Concept



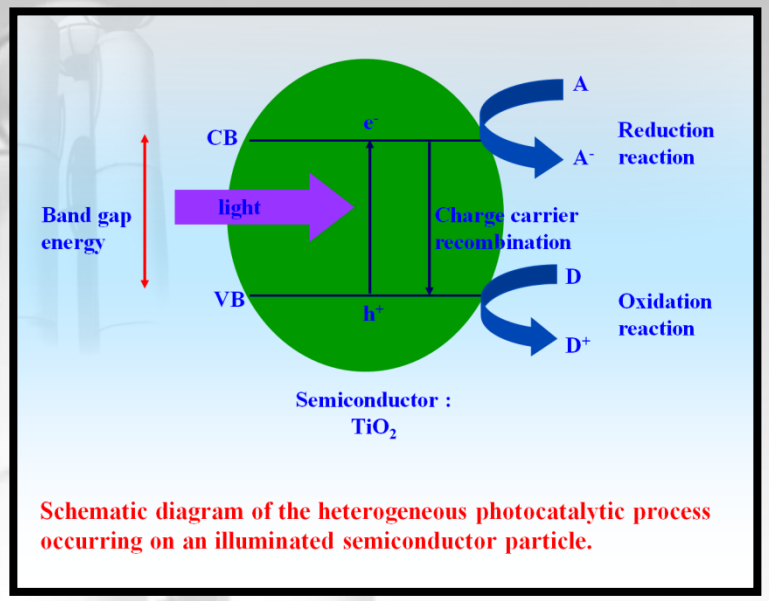
Light = λ < 385 nm

Photocatalyst = Titanium dioxide – nanoparticles, nanotubes, or thin films

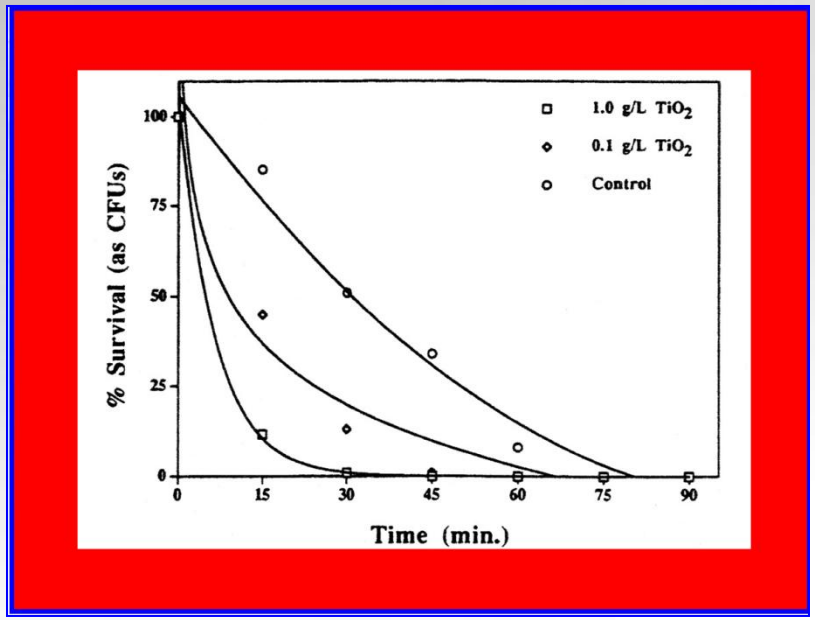
Reaction regimes: Photocatalytic < ~100 ^{0}C

Photo- and thermal catalytic ~100-200 ^{0}C

Thermal catalytic > 200 ^{0}C



Schematic diagram of the heterogeneous photocatalytic process occurring on an illuminated semiconductor particle.

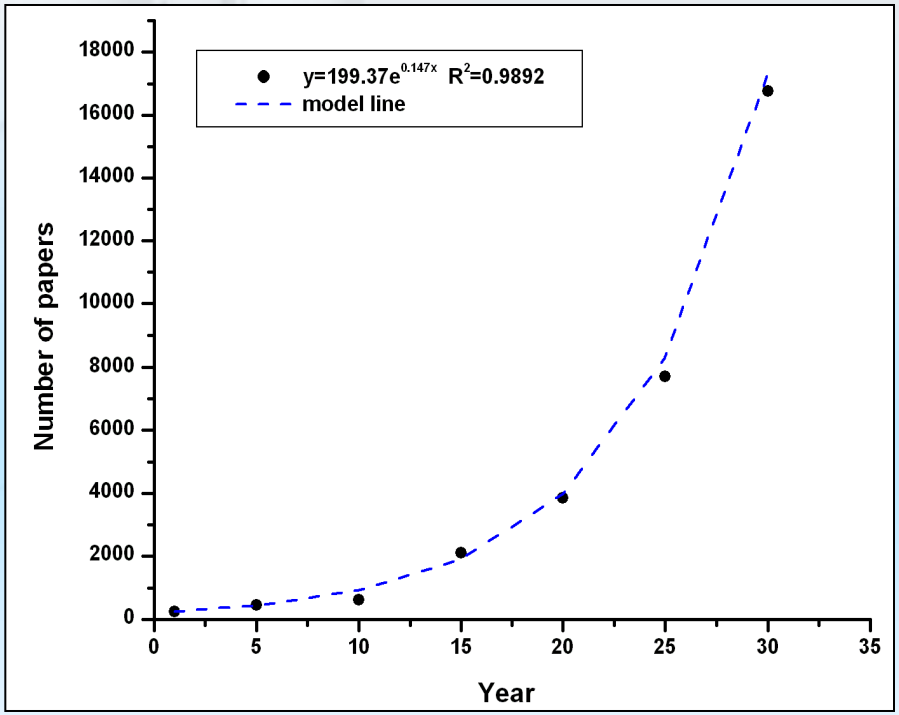


- Toxic metals or metalloids (Cr, Ni, As, Pb, Cd, Zn, Tl, Se)
- Microorganisms (*E. coli*)
- Organics (methylene blue, formaldehyde)

C. Wei , W. Y. Lin, Z. Zainal, N. E. Williams, K. Zhu, A. P. Kruzic, R. L. Smith, and K. Rajeshwar, *Environ. Sci. & Technol.* 28, 934-938 (1994).

K. Rajeshwar, C. R. Chenthamarakshan, S. Goeringer, and M. Djukic, *Pure & Appl. Chem.* 73, 1849-1860 (2002).

Ray Kurzweil's "law of accelerating returns": Technological progress happens exponentially and not linearly.



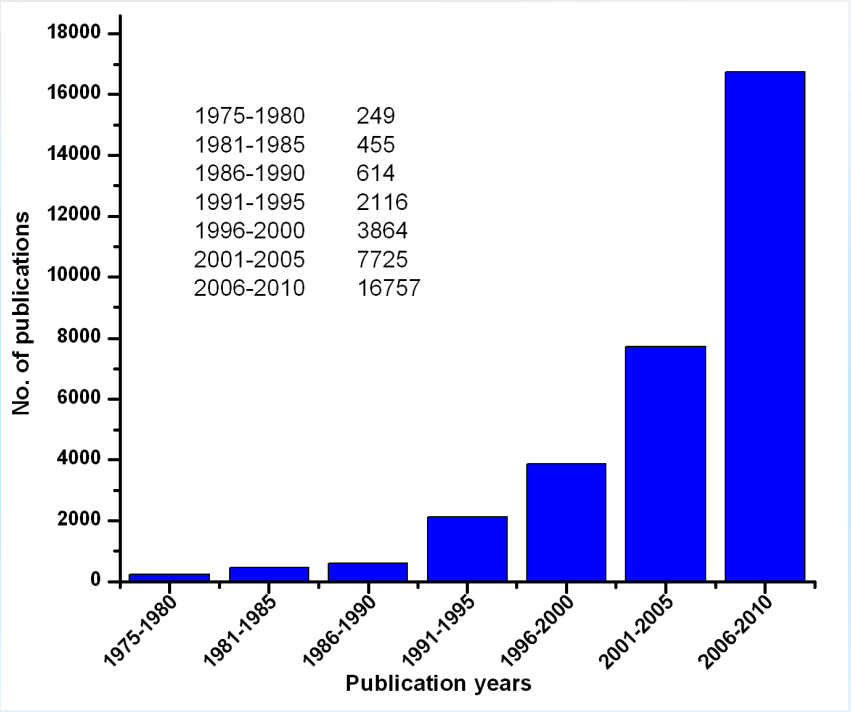
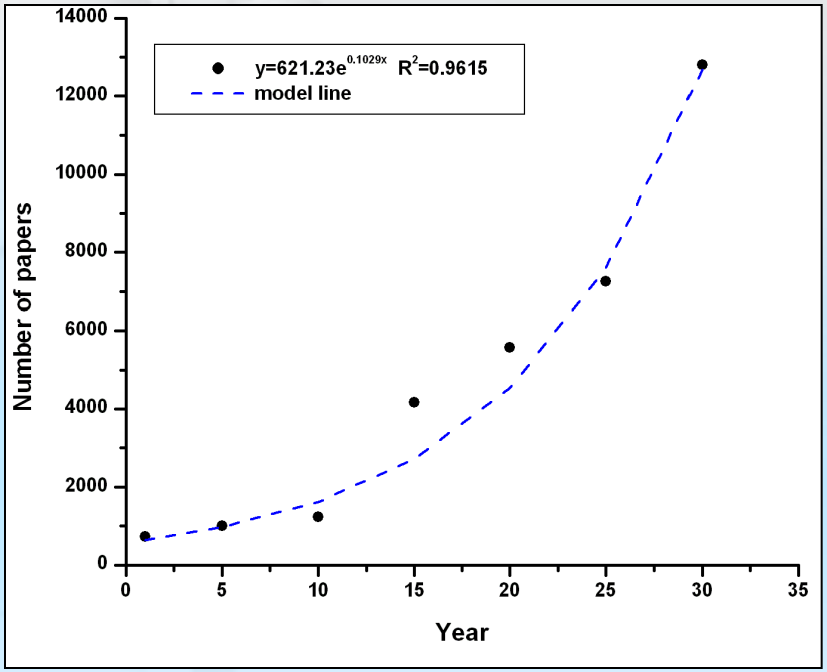
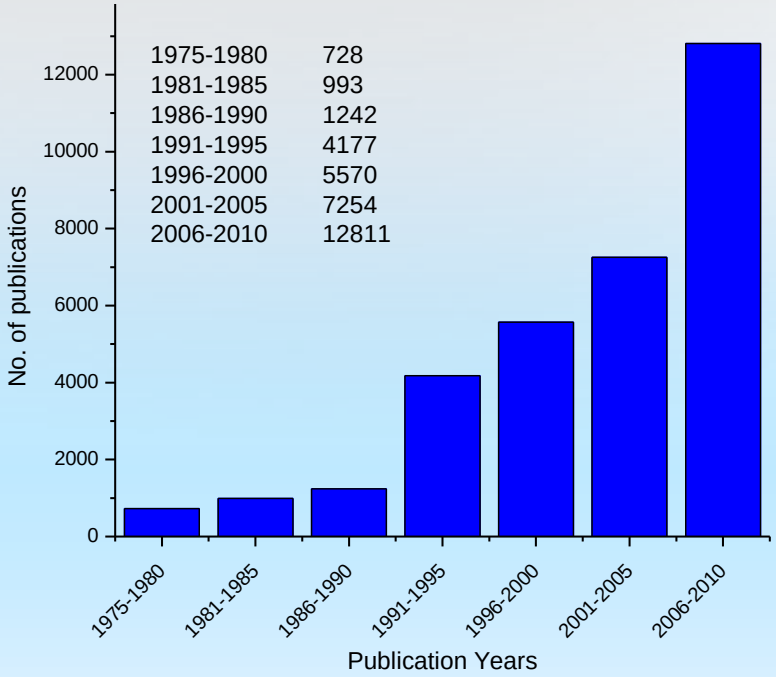


Figure 3. The results from a literature search using the ISI Web of Knowledge database using the keywords: "photocatalysis and TiO_2," "photocatalysis and oxide semiconductor," "photocatalysis and pollutant degradation." The related literature on "water splitting" and "dye-sensitized solar cell" was excluded from this database. The insert contains an exponential fit of the literature search results.





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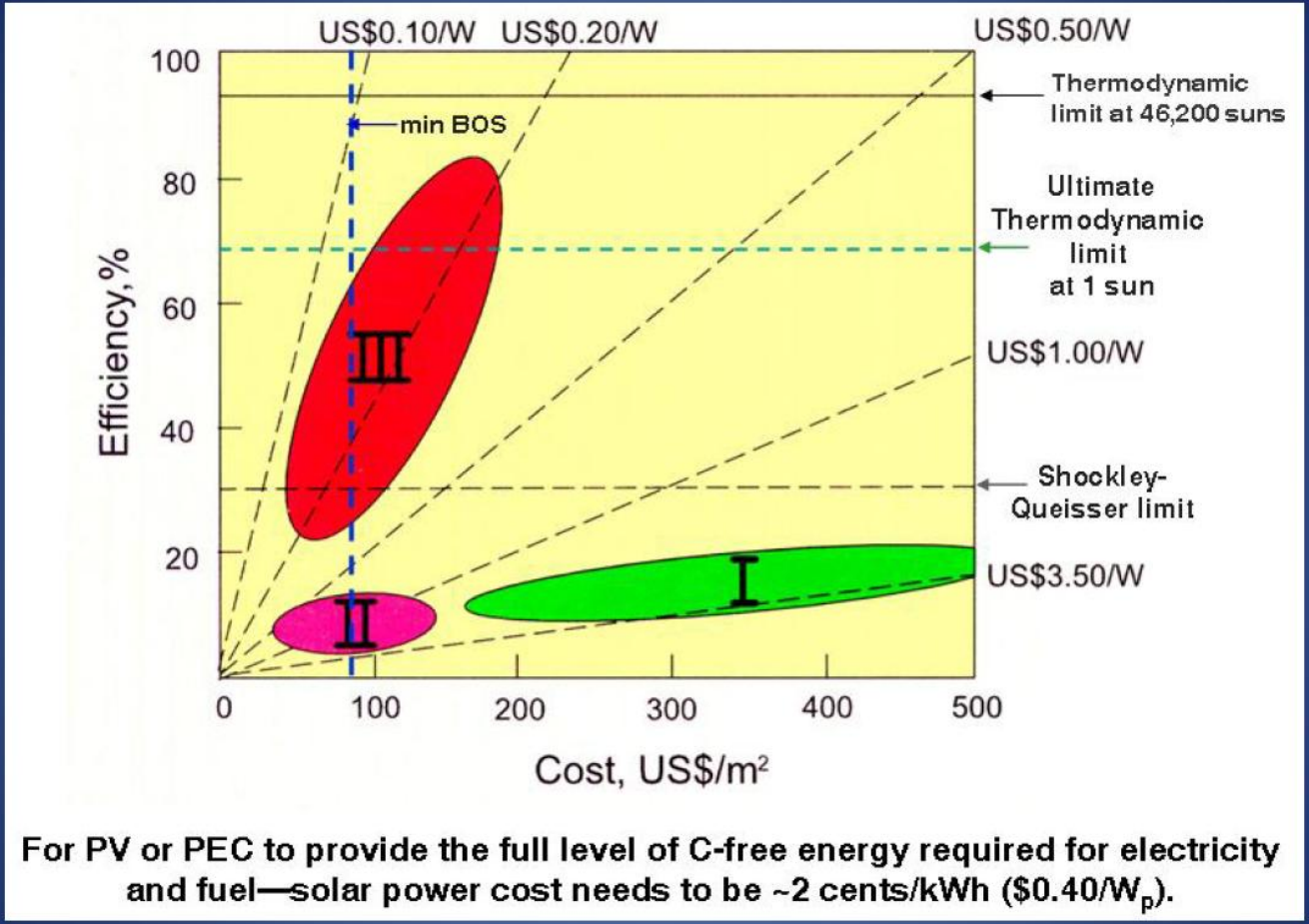
Generation	Materials
First-generation or 1G	Semiconductor single crystals
Second-generation or 2G	Polycrystalline thin films; metal-doped semiconductors for visible light sensitization; semiconductor powder suspensions for photocatalysis; semiconductor superlattice photoelectrodes
Third-generation or 3G	Nanostructured semiconductors and composites; size-quantized semiconductors (or quantum dots); semiconductor nanotubes and nanowires; semiconductor-conducting polymer composites; biomimetic architectures

K. Rajeshwar, *J. Phys. Chem. Lett.* (Guest Commentary) 2011, *2*, 1301-1309.

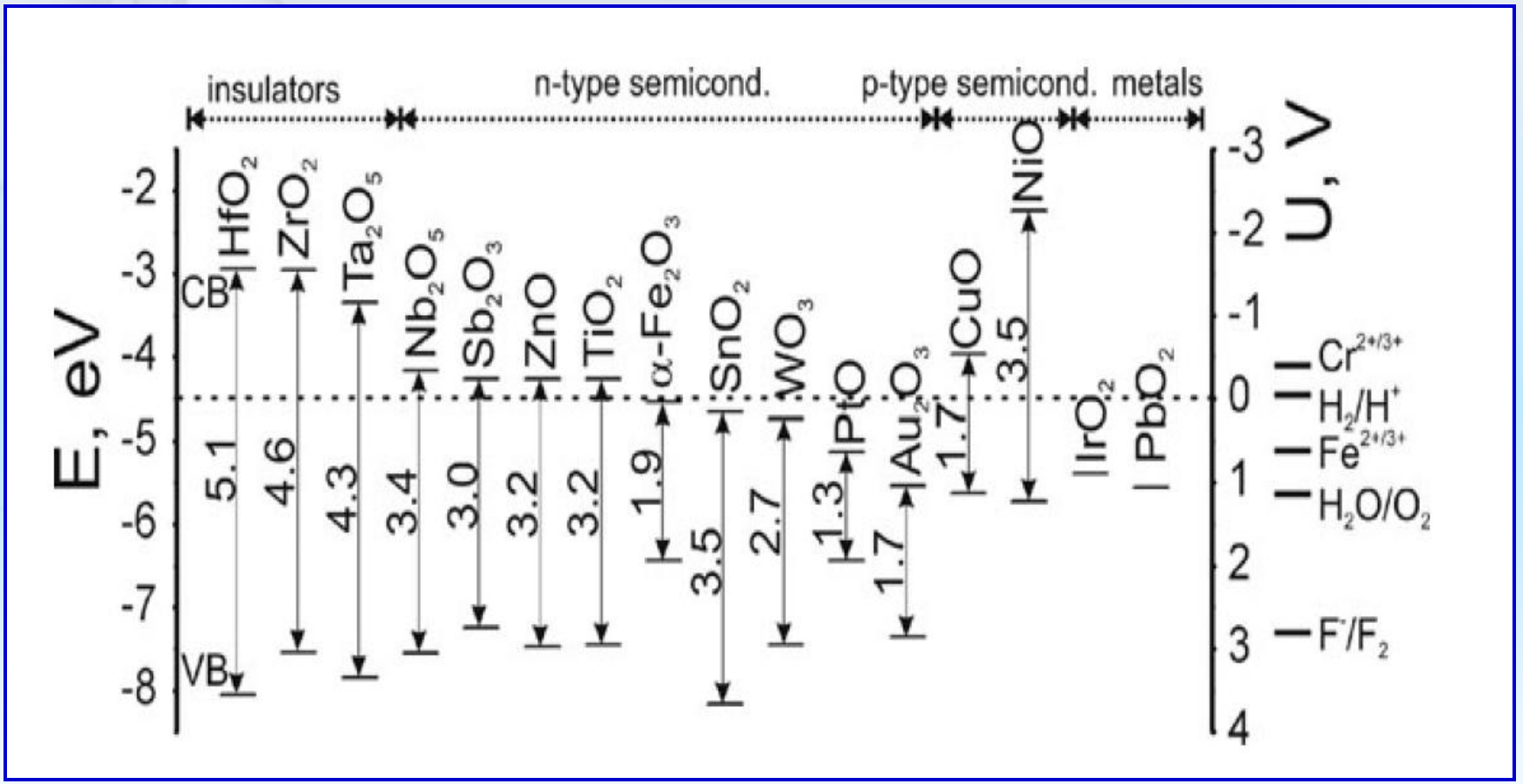


PV power costs ($/Wp) as function of module efficiency and areal cost (Source: M. Green, 2004)

The Ideal Photocatalyst: Holy Grail

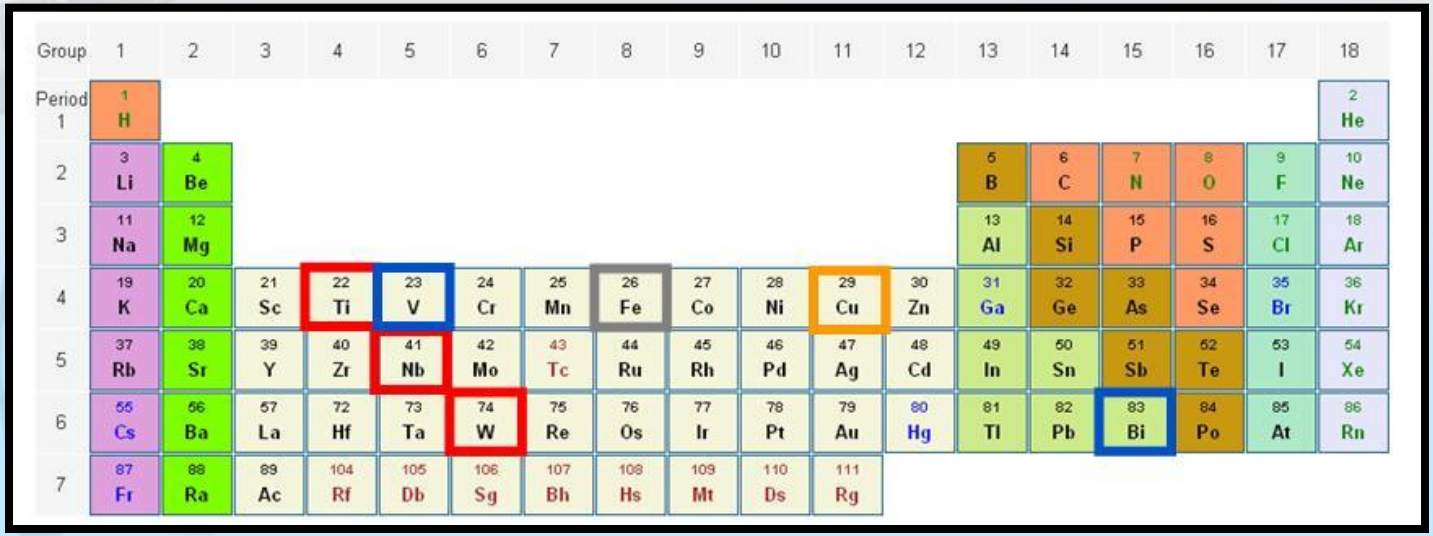
- Stable
- Good overlap of absorption cross-section with solar spectrum
- High conversion efficiency and quantum yield
- Compatible with a variety of substrates and reaction environments
- Low cost

AND THE SEARCH GOES ON…!



Ghicov, A.; Schmuki, P. *Chem. Commun.*, 2009, 2791 - 2808

Why Oxide Semiconductors?



Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period 1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg							

- **Component elements are plentiful and non-toxic contrasting with compounds such as GaAs, InP, CdTe, CdSe.**
- **Oxide semiconductors are usually photoelectrochemically stable in aqueous media.**
- **They have shown most promise for water photoelectrolysis application.**
- **Oxides can be easily doped and their opto-electronic properties modified.**

However, they are usually prepared by high-temperature (e.g., ceramic) routes.

Infusion of Ideas, People, Tools from Other Areas

- **High Tc Superconductivity – energized solid-state chemistry and oxide *semiconductor* prep.**
- **Colloid chemistry provided big fillip (e.g., Q-dots).**
- **Ultrafast (time-resolved) spectroscopy**
- **Nanotechnology (nanotubes, nanorods, nanowires etc)**
- **Electrocatalysis – note water splitting is fuel cell electrochemistry done in reverse!**

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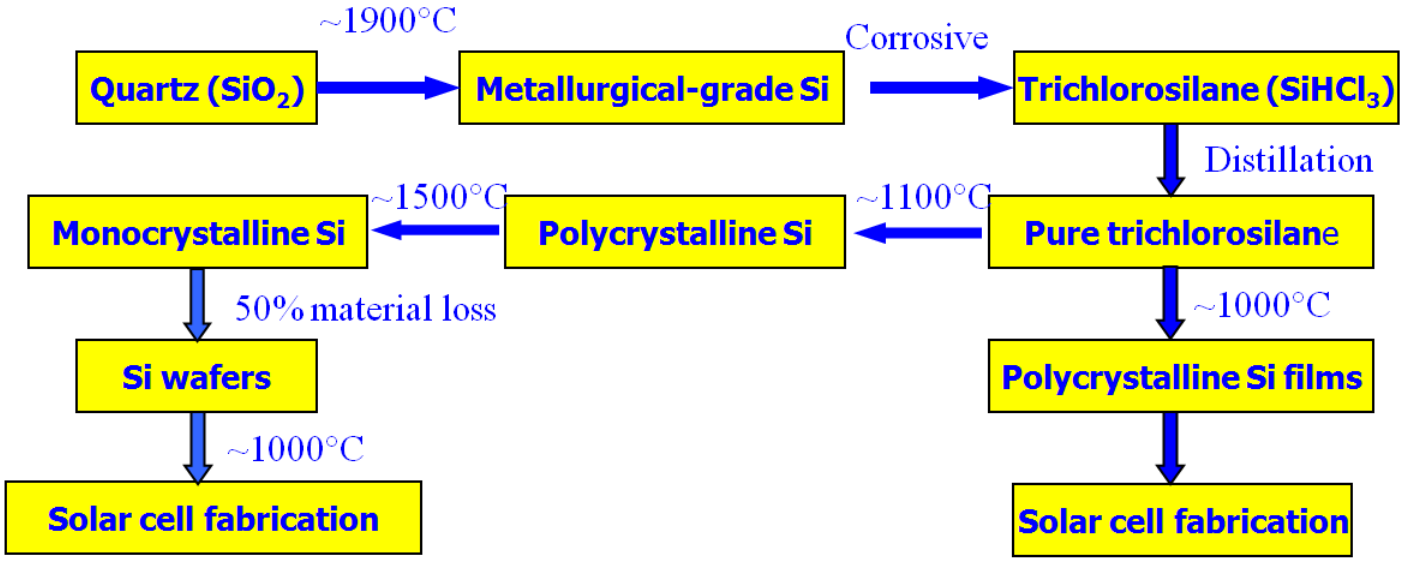
Time and Energy-Efficient Preparation Routes to Oxide Semiconductors

- Electrodeposition
- Sol-Gel Chemistry
- Chemical Bath Deposition
- Combustion Synthesis

Mild and Energy-Efficient Preparation & Processing Routes to Oxide Semiconductors



1st generation, bulk, monocrystalline Si solar cells

2nd generation, thin-film, polycrystalline Si solar cells

- **Process is energy-intensive.**
- **Energy payback time is long.**

$$EPBT = E_{input}/E_{saved}$$

Energy Payback Time: The time a solar cell takes to produce the same amount of energy we put in to fabricate it

Time and Energy-Efficient Preparation Routes to Oxide Semiconductors

- Electrodeposition
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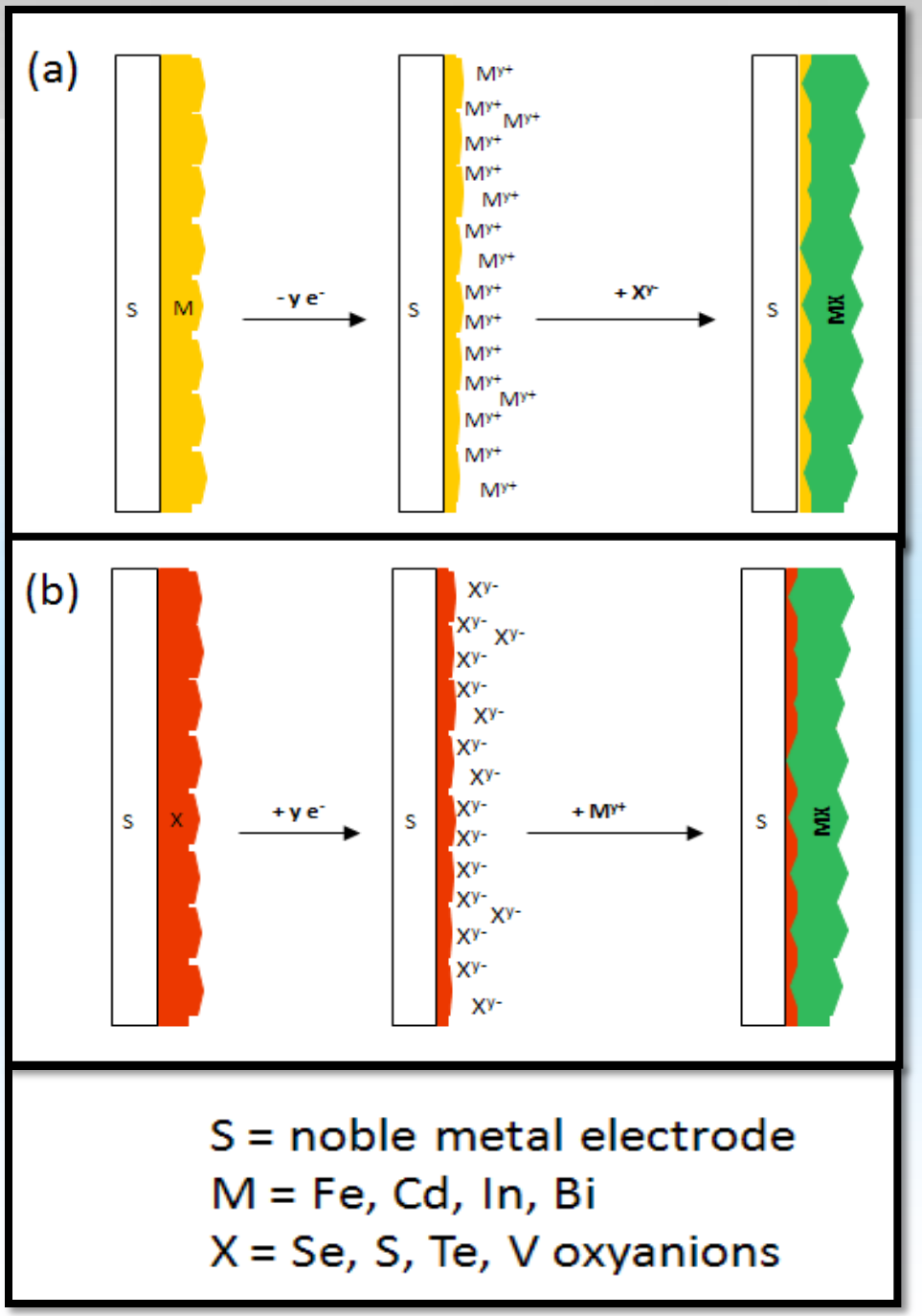
- Combustion Synthesis


(a)
S
M
- y e⁻
S
M^{y+}
+ X^{y-}
S
MX
(b)
S
X
+ y e⁻
S
X^{y-}
+ M^{y+}
S
MX
S = noble metal electrode
M = Fe, Cd, In, Bi
X = Se, S, Te, V oxyanions

THE JOURNAL OF PHYSICAL CHEMISTRY C

ARTICLE

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Tailoring Interfaces for Electrochemical Synthesis of Semiconductor Films: $BiVO_4$, Bi_2O_3, or Composites

Noseung Myung,[†] Sunyoung Ham,[‡] Seungun Choi,[†] Yujin Chae,[†] Whan-Gi Kim,[†] Young Jin Jeon,[†] Ki-Jung Paeng,[‡] Wilaiwan Chanmanee,[§] Norma R. de Tacconi,[*,§] and Krishnan Rajeshwar[§]

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[‡]Department of Applied Chemistry, Konkuk University Chungju Campus, Chungju, Chungbuk 380-701, Republic of Korea

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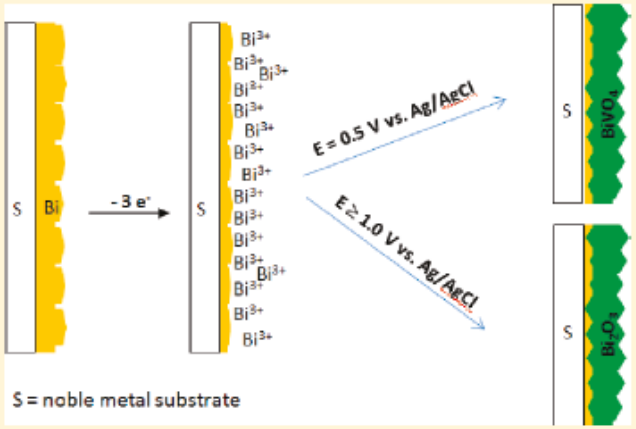
ABSTRACT: The mechanistic aspects of a two-step method for the electrodeposition of a $BiVO_4$ semiconductor (previously developed in the Rajeshwar/Tacconi laboratory) were elaborated by the combined application of voltammetry and EQCM. The electrosynthesized films were also characterized ex situ using SEM, EDX, XRD, and XPS. Stripping of pre-electrodeposited bismuth films, followed by reaction either with VO_4^{3-} (formed by hydrolysis from the initially added VO_3^- species) or with hydroxide ions, produced $BiVO_4$ or Bi_2O_3 thin films in situ on the Pt electrode. The deposition potential, pH of the electrolyte, and choice of vanadium precursor were shown to be crucial variables in the composition of the electrodeposited film. When a more positive potential than 0.5 V (vs Ag/AgCl reference) was applied to the Bi-modified electrode in VO_3^--containing electrolyte, the content of Bi_2O_3 in the film increased instead of $BiVO_4$. Stripping efficiency of the predeposited bismuth layer was increased at acidic electrolytes and resulted in higher $BiVO_4$ content in electrodeposited films, whereas hydrolytic conversion of VO_3^- to VO_4^{3-} was promoted in basic electrolytes. Formation of Bi_2O_3 was also favored by the use of alkaline electrolytes (e.g., pH 10) for the electrodeposition. Photoelectrochemical experiments showed the electrosynthesized $BiVO_4$ to be an n-type semiconductor, and reproducible photocurrents were obtained using a Na_2SO_4 supporting electrolyte.



Time and Energy-Efficient Preparation Routes to Oxide Semiconductors

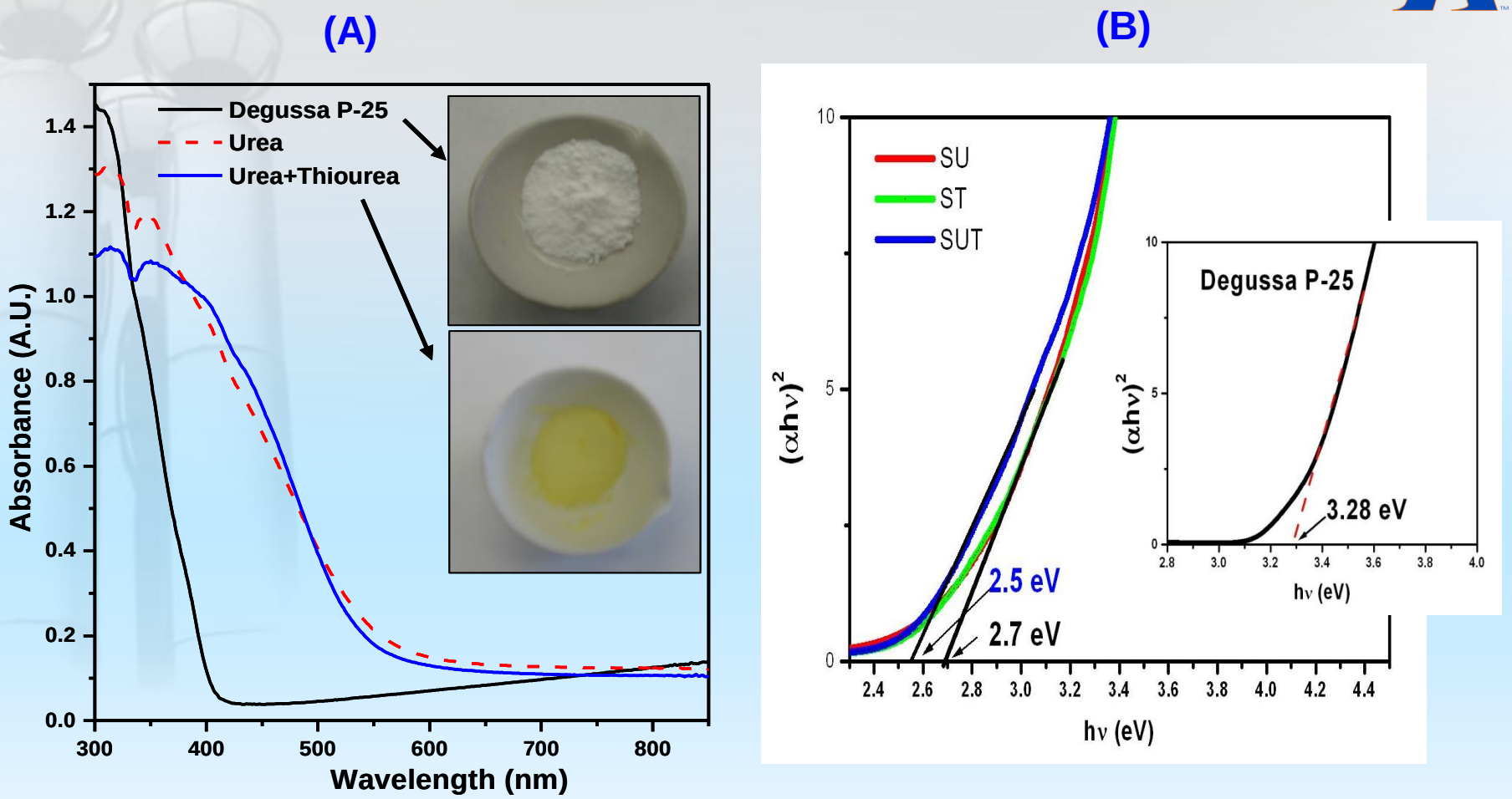
- Electrodeposition
- Sol-Gel Chemistry
- Chemical Bath Deposition
- Combustion Synthesis

Advantages of Combustion Synthesis

- Exothermic and fast reaction
- Products are homogenous and crystalline
- High surface area
- Simplicity of the process

  → No special equipment is required
- Possibility to incorporate dopants in situ in the oxide

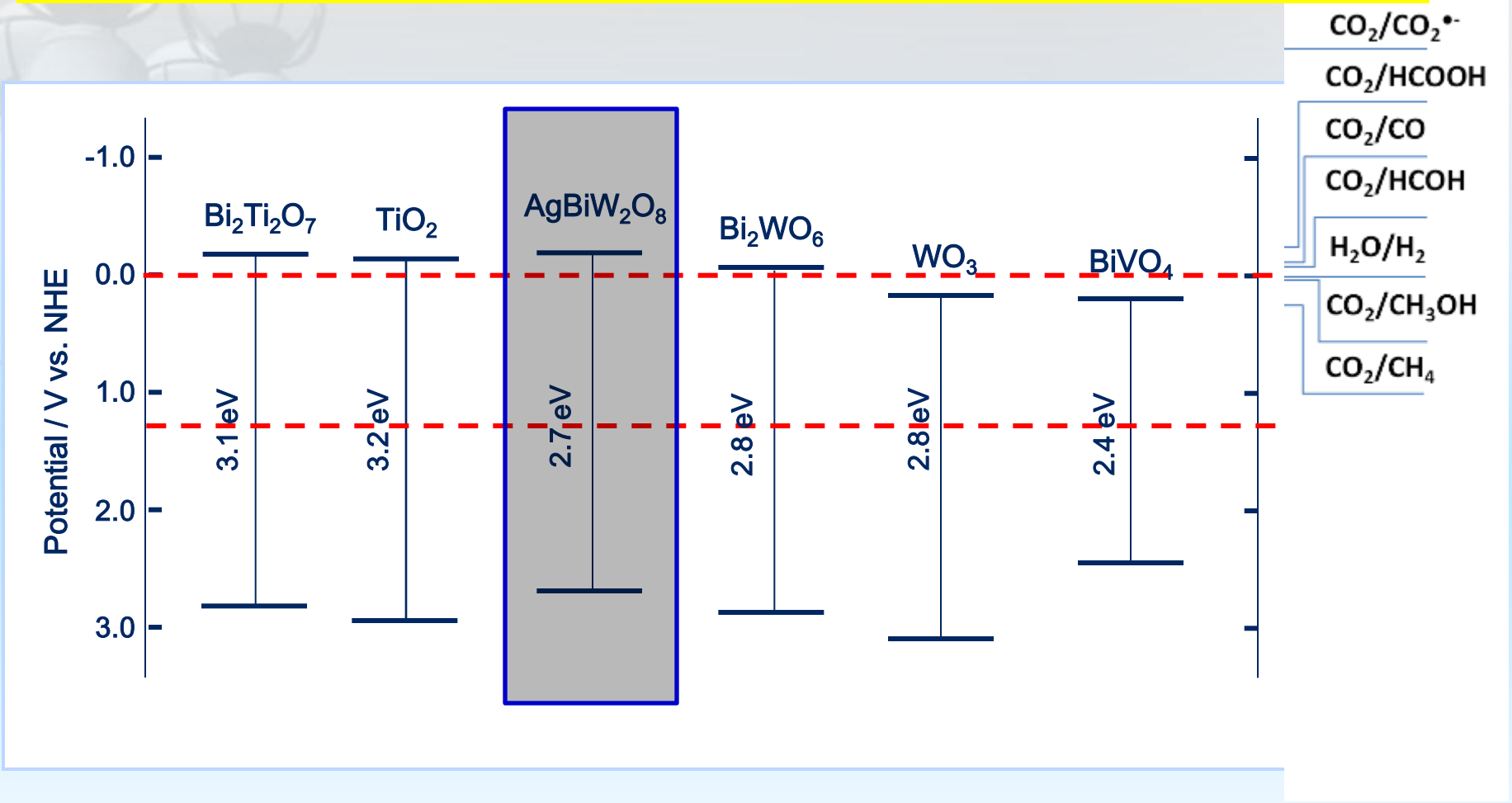
Energy input for synthesis process comes from reaction exothermicity



(A) Diffuse reflectance of TiO_2 samples prepared by combustion synthesis versus Degussa P-25 titania. A visual contrast of the benchmark TiO_2 with respect to combustion synthesized TiO_2 is given in the insert. (B) Corresponding Tauc plots for these TiO_2 samples. α is the absorption coefficient computed as a function of the energy (hν) from the UV-visible diffuse reflectance data in (A).

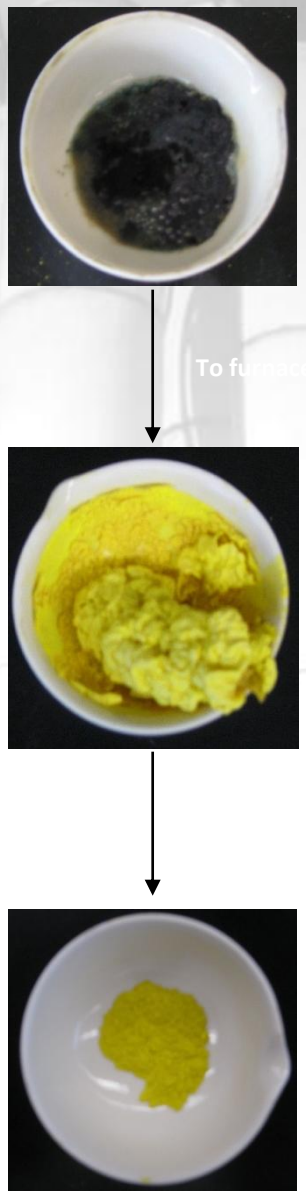
Rajeshwar, K.; de Tacconi, N. R. "Solution combustion synthesis of oxide semiconductors for solar energy conversion and environmental remediation," *Chem. Soc. Rev.* 38, 1984-1998 (2009).

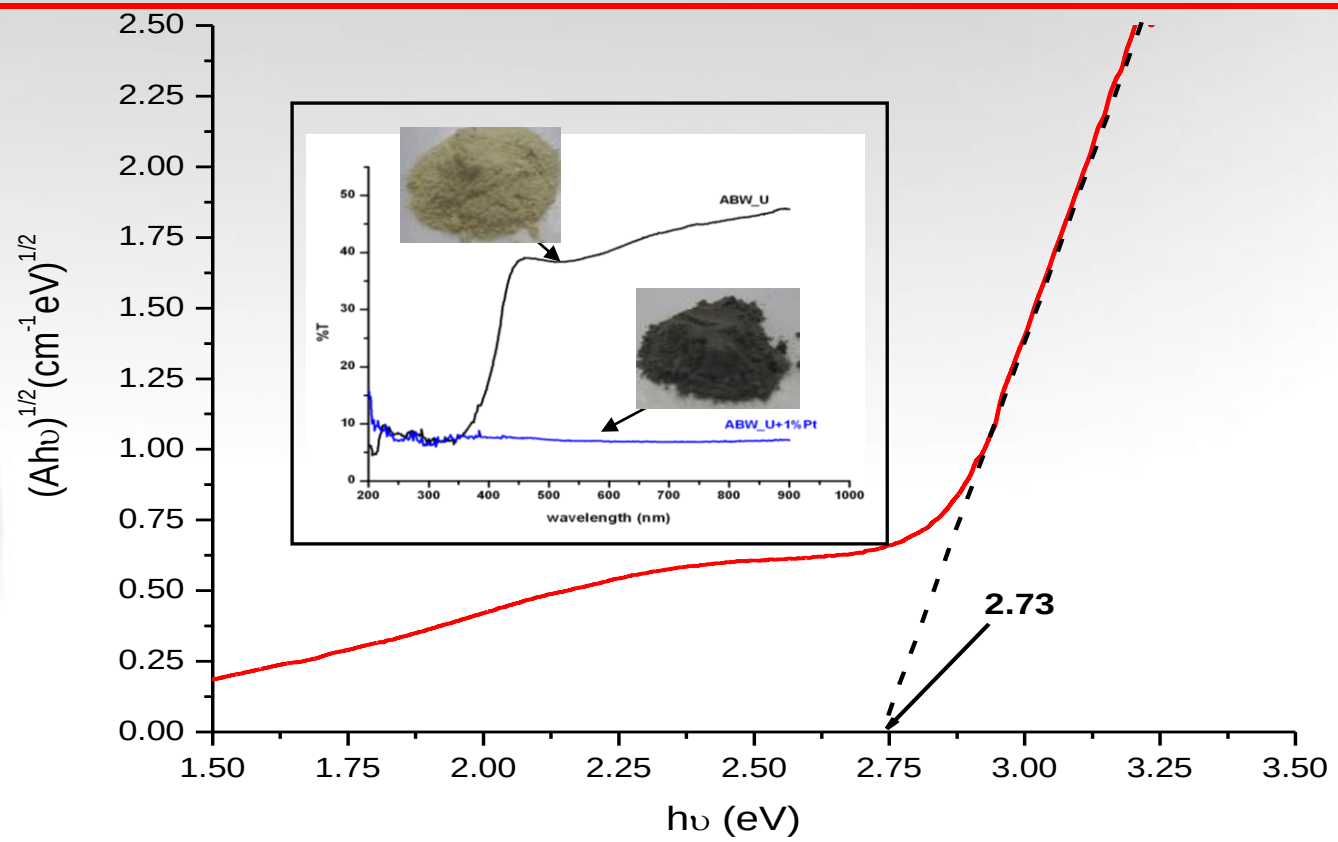
Selected Semiconductor Photocatalysts



Comparison between the band edges of selected semiconductors (at pH 1) and the redox potentials for water splitting.

Combustion Synthesis of $AgBiW_2O_8$





Tauc plot for combustion synthesized $AgBiW_2O_8$. The inset show the percent transmittance data of the sample before (black line) and after photodeposition of 1wt % Pt (blue line), along with the corresponding sample photographs

N. R. Tacconi, H. K. Timmaji, W. Chanmanee, M. N. Huda, P. Sarker, and K. Rajeshwar, *J. Am. Chem. Soc.* (submitted).

Characterization of $AgBiW_2O_8$

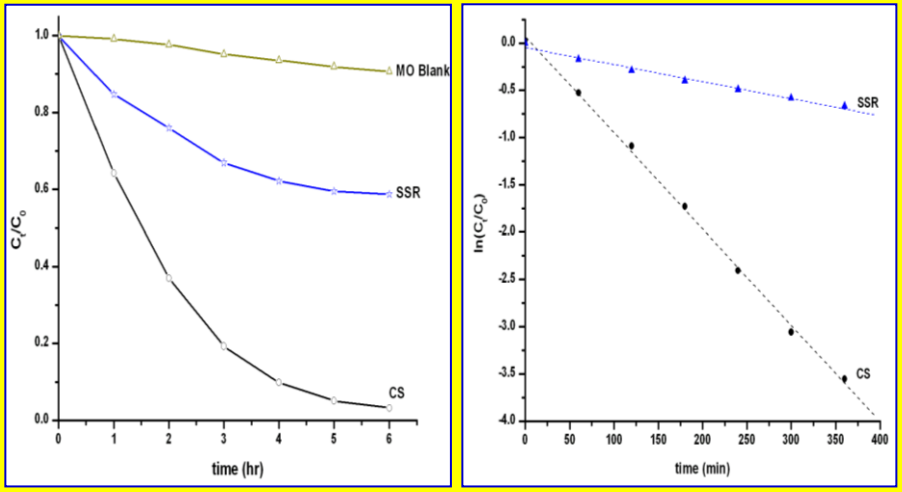
SURFACE AREA (BET)

Photocatalyst	Micropore Area (cm^2)	External Surface Area (cm^2)	BET Surface Area ($m^2\ g^{-1}$)
SCS $AgBiW_2O_8$	5.488	28.938	34.44[a]
SSR $AgBiW_2O_8$	0.136	0.406	0.54[a]
SSR $AgBiW_2O_8$	-	-	0.29[b]

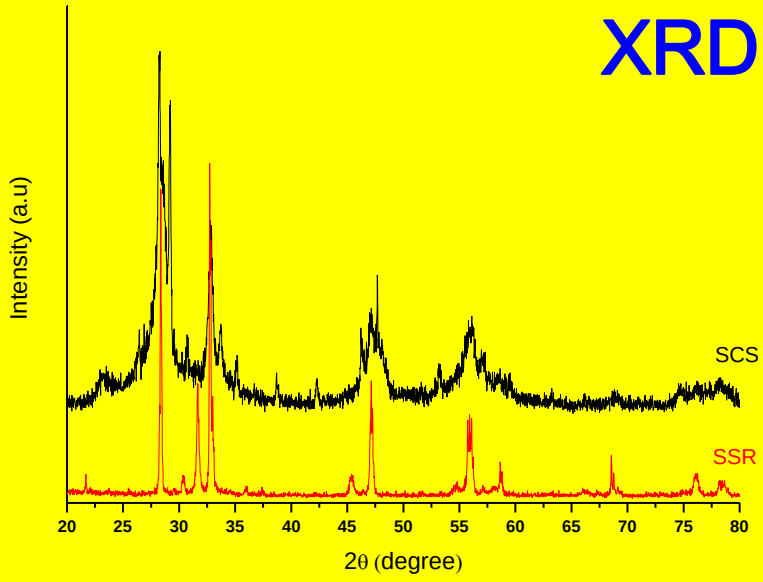
a)Our data
b)Tang, J.; Ye, J. *J. Mater. Chem.* 2005, *15*, 4246

Combustion synthesis affords a better quality product in a time- and energy- efficient manner, as compared to the solid state procedure.

Photocatalytic Activity



XRD



CS $AgBiW_2O_8$ nanoparticles are in the 5 – 10 nm size range according to HRTEM and XRD.

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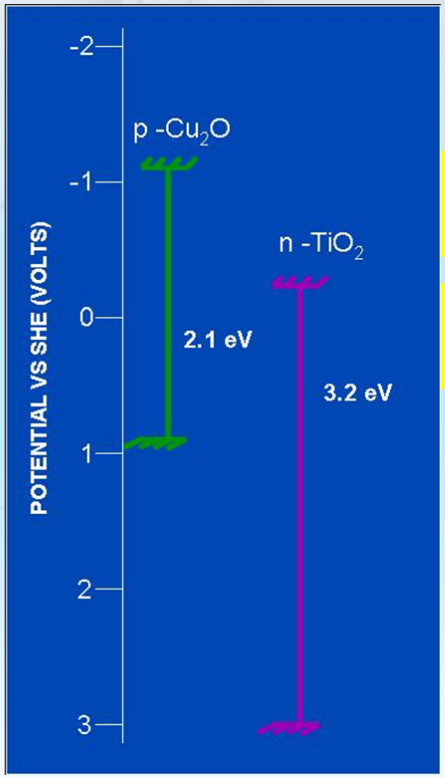
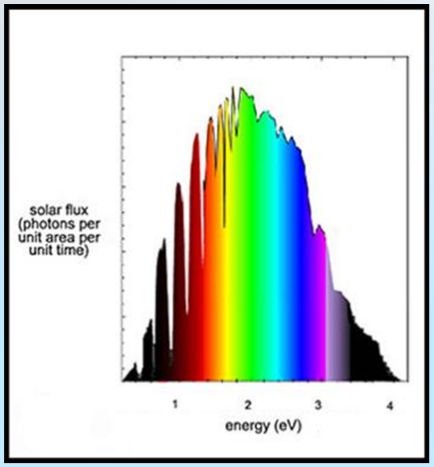
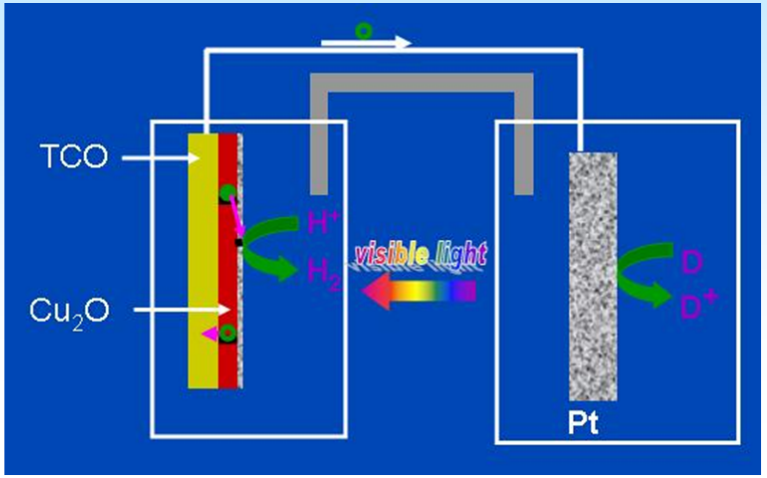
Kill Two Birds With a Stone (Sunlight)



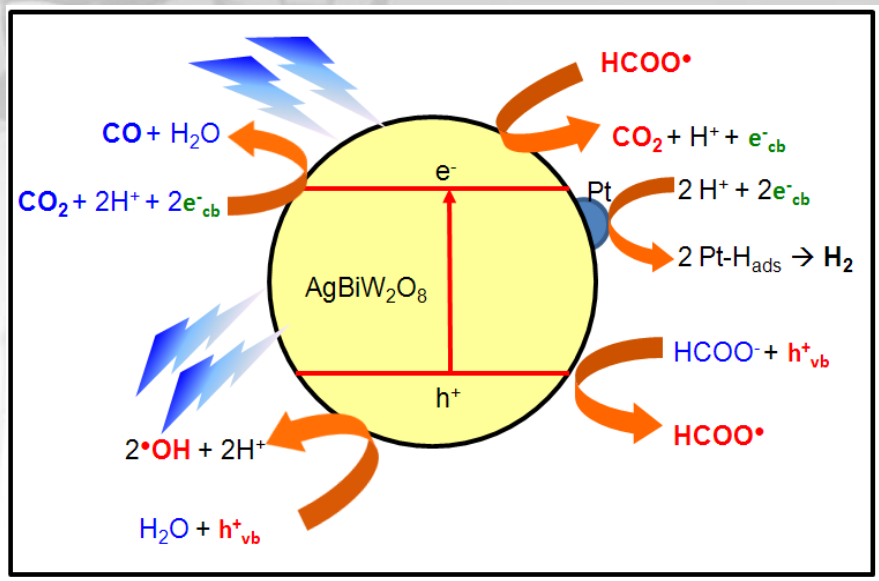
- **Make hydrogen**
- **Destroy pollutant**

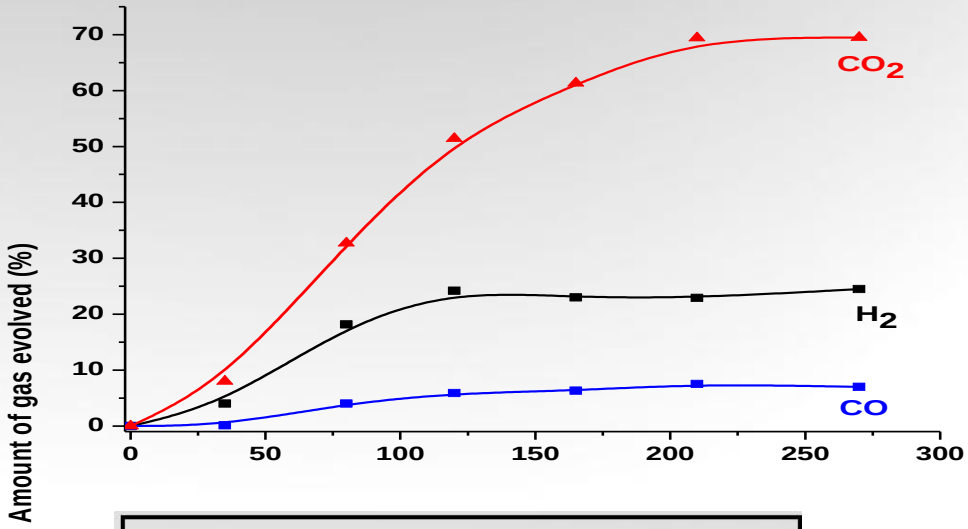




S. Somasundaram, C.R. Chenthamarakshan, N.R. de Tacconi, K. Rajeshwar, *Int. J. Hydrogen Energy* **2007**, *32*, 4661.

Photogeneration of Syngas from Formic Acid





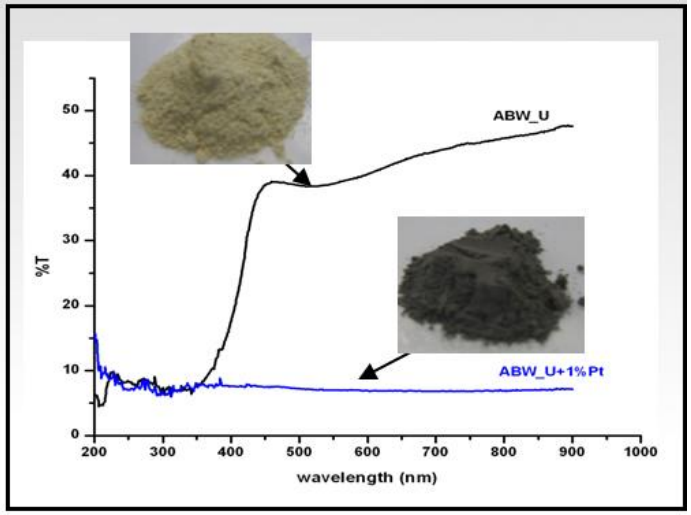
$HCOO^- + h^+_{vb} \leftrightarrows HCOO^\bullet$

$HCOO^\bullet \rightarrow H^\bullet + CO_2$

$CO_2 \xrightarrow{k(3)} H^+, e^-_{cb} \rightarrow CO$

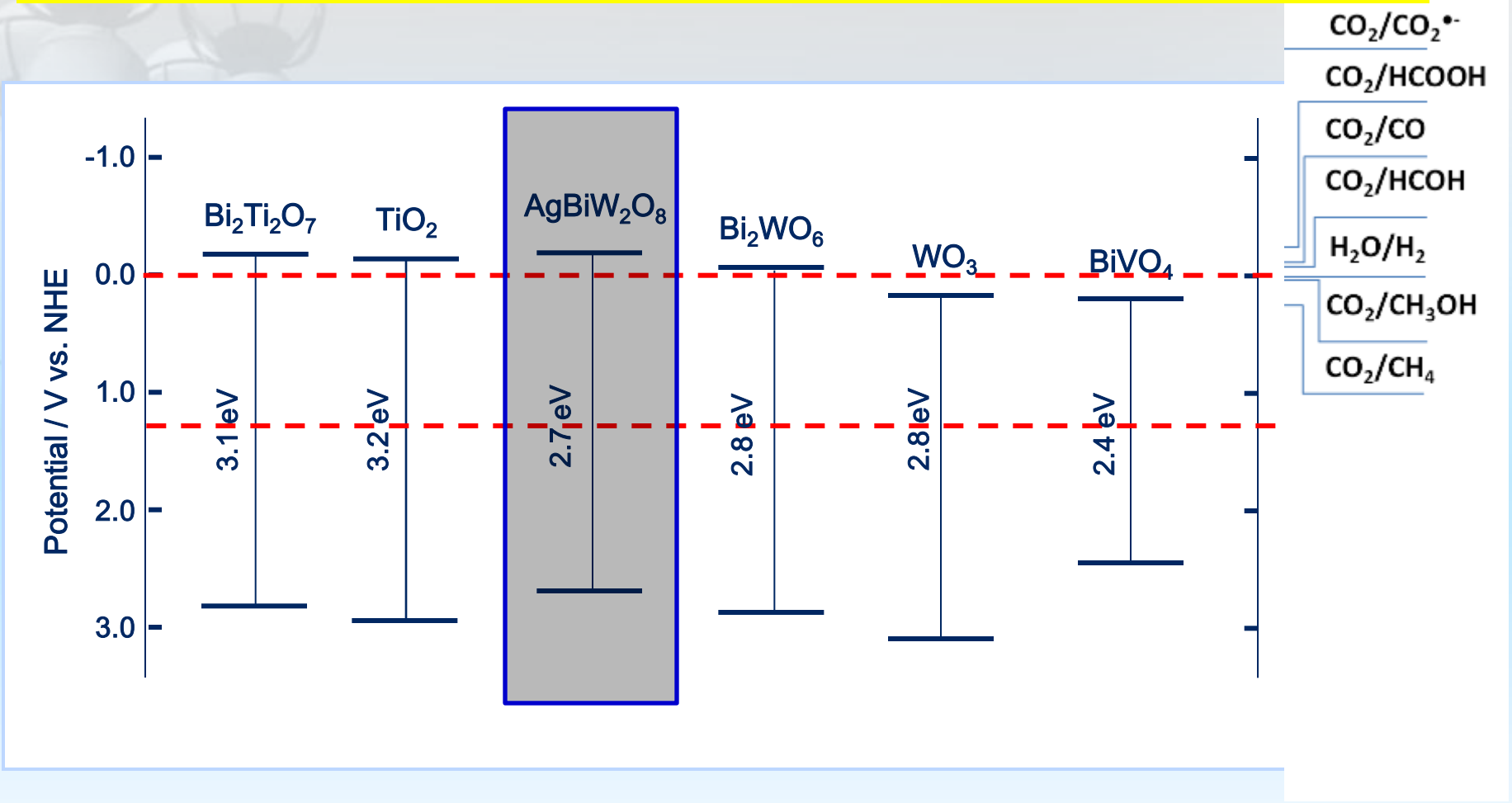
$CO_2 \xrightarrow{k(2)} Pt \downarrow H^+, e^-_{cb} \rightarrow H_2$

$2H^+ + 2\,e^-_{cb}(Pt) \xrightarrow{k(4)} 2Pt\text{-}H_{ads} \rightarrow H_2$



N. R. Tacconi, H. K. Timmaji, W. Chanmanee, M. N. Huda, P. Sarker, and K. Rajeshwar, *J. Am. Chem. Soc.* (submitted).

Selected Semiconductor Photocatalysts



Comparison between the band edges of selected semiconductors (at pH 1) and the redox potentials for water splitting.

Concluding Perspectives

After 30-odd years, no commercial process yet.

Chemical engineers have barely entered the fray.

Efficiencies have to climb (>10-15%) before they will?

Contrast with success stories, e.g., lithium ion batteries, solid oxide fuel cells.

The Platinum Curse: e.g., PEMFCs?

Thank you for listening!