Chemical Sciences for Energy Storage: A Societal Challenge

Niyazi Serdar SARICIFTCI
Linz Institute for Organic Solar Cells (LIOS),
Institute for Physical Chemistry, Johannes Kepler University Linz, Austria
www.lios.at
Happy Life

Energy Resources
Our planet will be warmer
Can we get rid of CO2?

**CO$_2$-Einlagerung**

Carbon sequestration rates to produce 10 TW CO$_2$-emission-free from fossil fuels

- Biomass fuel to central power plants
- Electricity & H$_2$
- Magnesium carbonate bricks
- CO$_2$ capture from fossil fuels
- Sequestered CO$_2$
- Deep coal beds, subterranean aquifers
- Ocean release of CO$_2$/CaCO$_3$ mixture or liquid CO$_2$
- Farm residue or marine biomass sunk to deep ocean
Methanol as carrier and storage of energy

a.) Methanol can be mixed to gasoline

b.) Methanol is used in fuel cells

c.) Methanol is starting chemical for Many other derivatives

George Olah, Nobel Prize 1994
Univ. of Southern California, USA
Linz Institute for Organic Solar Cells

Physics of Organic Semiconductors:
1.) Photoexcited spectroscopy
2.) Photoconductivity
3.) Thin film characterization
4.) Nanoscale engineering
5.) Nanoscale microscopy (AFM, STM...)
6.) In situ spectro-electrochemistry

Organic/Hybrid Solar Cells
CO2 Recycling into Synthetic Fuels
Spectroscopy and Electrochemistry
Bio-Organic Electronic Devices

„Incubator“ for small high tech spin-off companies
LIOS @ JKU is #14 in the world ranking of material scientists (Thomson Reuters, March 2011)
Acknowledgements

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CONJUGATED POLYMER - ACCEPTOR HETEROJUNCTIONS; DIODES, PHOTODIODES, AND PHOTOVOLTAIC CELLS

Inventors: N. S. Sariciftci; Alan J. Heeger, both of Santa Barbara, Calif.

Assignee: The Regents of the University of California, Oakland, Calif.

Filed: Aug. 17, 1992

Int. Cl. .......................... H01L 29/28
U.S. Cl. ......................... 257/40; 257/184; 257/461; 136/263
Field of Search ...................... 257/40, 184, 461; 365/215; 136/263

References Cited
U.S. PATENT DOCUMENTS
5,171,373 12/1992 Hebard et al. .......................... 257/40

OTHER PUBLICATIONS
Kamat, P. “Photoinduced Charge Transfer Between


Primary Examiner—Sara W. Crane
Attorney, Agent, or Firm—Morrison & Foerster

ABSTRACT
This invention relates generally to the fabrication of heterojunction diodes from semiconducting (conjugated) polymers and acceptors such as, for example, fullerenes, particularly Buckminsterfullerenes, C_{60}, and more particularly to the use of such heterojunction structures as photodiodes and as photovoltaic cells.
We claim as our Invention:
1. A heterojunction device comprising
   a. a layer of a conjugated polymer which serves as a donor, and adjacent thereto, a
   b. layer of an acceptor material comprising an acceptor selected from the group consisting of the group of fullerenes, substituted fullerenes, fullerene derivatives, polymers comprising fullerenes or substituted fullerenes or of organic or polymeric acceptors having electronegativity in the range to enable a photoinitiated charge separation process defined
3. A heterojunction device comprising
   a. a conjugated polymer which serves as a donor, and adjacent thereto,
   b. an acceptor material comprising an acceptor selected from the group consisting of fullerenes or fullerene derivatives, polymers comprising fullerenes or fullerene derivatives, organic and or polymeric acceptors having electronegativity in the range to enable a photoinitiated charge separation where
   donor (D) and acceptor (A) units are either covalently bound (intramolecular), or spatially close but not covalently bonded (intermolecular); “1,3” denotes singlet or triplet excited states, respectively,
   and where a heterojunction between the conjugated polymer and acceptor material is formed in situ by controlled segregation during solidification from a solution containing both the donor and the acceptor moieties.
Roll to roll produced solar cells

Konarka Inc.
Ultrathin, shrinkable, stretchable organic solar cells

Martin Kaltenbrunner, Matthew White et al. Nature Comm. DOI: 10.1038/ncomms1772 April, 2012
Ultrathin and lightweight organic solar cells with high flexibility

Martin Kaltenbrunner1,2,3, Matthew S. White4, Eric D. Glowaicki4, Tsuyoshi Sekitan2,4, Takao Someya2,4, Niyazi Serdar Sariciftci5 & Siegfried Bauer1
Textile integrated organic solar cells fibers

Solar cell integrated textiles

A commercial solar jacket and bag

www.scottevest.com  www.neubers.de
“Optimum“ Geometry for Organic and Hybrid Solar Cells

High workfunction electrode

Organic p-type conductor (donor)

Organic n-type conductor (acceptor)

Low workfunction electrode
CHEMISTRY BASED SOLAR CELLS
REACH >10%

Aramaki et al,
Mitsubishi Chemicals Labs, Tokyo
What is the next challenge in Solar Energy Conversion?

Solar energy STORAGE into chemical energy
Storage-Transport Problem

Space

Transport

Energy

Consumption Somewhere else

Energy Conversion

Consumption later and somewhere else

Consumption later

Storage of Energy

Transportable fuel created by solar energy conversion !!!
Unstability in Wind Energy Supply

Windeinspeisung
E.ON Transpower Netz Juni 2009
Installierte Kapazität 8.100 MW

Needs Buffering
Schwankung zwischen 0% und 100%
PV Deutschland: Durchschnitt 10%

Jahresgang 2008
Norddeutschland: Kreis 3xxxx
(normiert auf 1 kWp)
The problem: power fluctuation during generation and use

Batteries are slow, not suitable for power handling

The solution: Supercapacitors

G. Gruner, UCLA
Interfacing two R&D worlds

INTERFACE BETWEEN CO2 REDUCTION AND RENEWABLE ENERGY CREATION

CO2 EMISSIONS
CLIMATE CHANGES

RECYCLE CO2 !!!
CREATE FUEL

RENEWABLE ENERGIES

Future recycling of CO2 as important mission of renewable energies
$CO_2$ from air

$CO_2$ Capture

$CO_2$ Release

Reduction of $CO_2$ into a Fuel

Fuel
http://www.solar-fuel.net/
CO₂ Neutral Synthetic Fuels

Das Prinzip unseres CO₂-Kreislaufs

Kunde tankt regenerativ erzeugten Kraftstoff

Während der Fahrzeugnutzung: Ausstoß des gebundenen CO₂

In der Kraftstoffherstellung: Bindung von CO₂

Nutzung von CO₂ als Rohstoff

Courtesy Dr. Pengg
Natural Photosynthesis
Recycling of CO$_2$

Over 90 % of emitted CO$_2$ is generated by energy products.

To convert back CO$_2$ to fuels hydrogen or energy is required.

One promising field in this direction is the **photochemical** or electrochemical reduction of carbon dioxide using solar light.
IS IT POSSIBLE TO RECYCLE CO$_2$?

The answer is yes!

\[ \text{CO}_2 + 2e^- + 2H^+ \rightarrow \text{HCOOH} \quad (1) \]
\[ \text{HCOOH} + 2e^- + 2H^+ \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O} \quad (2) \]
\[ \text{CH}_2\text{O} + 2e^- + 2H^+ \rightarrow \text{CH}_3\text{OH} \quad (3) \]
\[ \text{CH}_3\text{OH} + 2e^- + 2H^+ \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad (4) \]

Steps in methanol oxidation/production.

Overall: 6e- process
\[ \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6e^- \]

Biocatalysis
Photocatalysis
Electrocatalysis
Inverse Fuel Cells

CH₄

O₂

Solar Energy

Inverse Fuel Cell Operation using Renewable Energies

CO₂

H₂O
Methanol as carrier and storage of energy

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George Olah, Nobel Prize 1994
Univ. of Southern California, USA
Photochemical Reduction of CO2

Homogeneous photocatalysts as well as electrocatalyst, Oppelt, Portenkirchner 2011

Journal of Organometallic Chemistry 696 (2011), 2252
Electrochemical reduction of CO$_2$

- Excess electric energy can be conveniently used for the catalysed reduction of CO$_2$ in water to afford alcohols and/or C$_n$-hydrocarbons: storage of electricity!

- Such use of excess electric energy can play a key role in the short term for the conversion of CO$_2$ into fuels implementing a significant recycling of carbon.

- The use of solar energy for CO$_2$ reduction in water is a key issue for the medium term: a substantial recycling of carbon could be performed.
Photocatalytic reduction of CO$_2$

1. Ru(bpy)$_3^{2+}$ (bpy = 2,2’-bipyridine) as both photosensitizer and catalyst

2. Ru(bpy)$_3^{2+}$ as the photosensitizer and another metal complex as the catalyst

3. ReX(CO)$_3$(bpy) ($X =$ halide or phosphine-type ligand) or a similar complex as both photosensitizer and catalyst

4. Ru(bpy)$_3^{2+}$ or Ru(bpy)$_3^{2+}$-type complex as the photosensitizer in micro-heterogeneous systems

5. A metalloporphyrin as both the photosensitizer and the catalyst

6. Organic photosensitizers with transition-metal complexes as catalysts

Coupling Chemistry and Biotechnology:

- \( \text{CO}_2 \text{aq} \rightarrow \text{HCOO}^- \) \( \rightarrow \) Formate dehydrogenase
- \( \text{HCOO}^- \rightarrow \text{H}_2\text{CO} \) \( \rightarrow \) Formaldehyde dehydrogenase
- \( \text{H}_2\text{CO} \rightarrow \text{CH}_3\text{OH} \) \( \rightarrow \) Methanol dehydrogenase

- NAD\(^+\)/NADH is the source of energy.
- Key issue: how to reverse the NAD\(^+\)/NADH couple after oxidation?
- Use of chemical systems for solar light harvesting and conversion.
Scheme of the enzymatic reduction of CO₂

**Reaction conditions**

Solution buffered at pH 7

- T = 37 °C
- P = 1 atm
4 mL of solution of Sodium Alginate 2% (m/v) in deionized water

1.6 mL TEOS

1 mL solution

F_{ato} DH (10.0 mg) F_{ide} DH (10.0 mg) ADH (10.0 mg)

In buffer TRIS-HCl 0.1 M (pH 7)

Drop by drop addition in 20 mL \( \text{CaCl}_2 0.2 \text{ M+TESO} \)

Sol-gel-formation time 30 min

Filtration

Washing with water

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Michele Aresta, Bari, Italy
Bulk Heterojunction Electrodes in Photoelectrochemical CO2 Recycling
Photoinduced Charge Generation

Photoinduced Redox Chemistry
sign our petition
Petition for using the solar energy for a peaceful, democratic future for the world

We, the undersigned to this letter, wish to emphasize the potential contribution of solar energy to a peaceful and democratic future for our planet.

Energy is essential for the development of human society. It is the right of every human to have access to energy sources for sustaining a dignified standard of living. With fossil fuels as the dominant source of energy in modern societies, being depleted at an alarming pace, energy becomes a commodity for those who can afford it. Hundreds of millions of people in the developing world have no access to affordable energy for a sustainable life. Even the developed countries have to spend a major part of their national income for importing fossil fuels. This dependency imposes a heavy economic burden and associated volatility. Today human society looks like a “fossil fuel addict” throwing away its future.
sign our petition

The control of fossil fuel supplies by a few corporations at both the international and national levels permits an oligarchy to undermine any true democracy in future.

In contrast to nuclear and fossil energies, which are associated with catastrophes, wars, inequality and power politics, solar energy is correlated with a peaceful, clean, democratic, green and sustainable future for mankind. Solar energy can never be monopolized. Human society needs decentralized solar energy for realization of global democratization. With energy independence and autonomy through solar energy, the world will have a better prospect to realize global democratization and prosperity and to ensure harmony among regions, nations and people. Solar light is widely distributed on our planet and has the capacity of providing many orders of magnitude more energy than we consume as a human society today.

With this motivation in mind the delegates of the conference “Solar Energy for World Peace” (www.solar4peace.org) came together in Istanbul to exchange scientific information on new solar energy technologies. A particular aim of this meeting has been the transfer of know how to the developing countries in Africa and the Middle East, with emphasis on the need for mutual cooperation at the scientific and technical levels in order to make this technology available to every human being on earth with equal rights to this free source of energy.
The undersigned participants request responsible persons at all national and international political levels to support the research, development and dissemination of solar energy. As scientists and engineers, we will strive to create the sciences and technologies needed to harvest and utilize solar energy economically for all people on our planet. The future of human society and of our planet will depend upon the widespread use of solar energy as an abundant, free and clean source of energy.
Future is…

Convergence of multiple crisis conditions:

1.) Energy crisis (oil running out)
2.) Climate crisis (CO2 and global warming)
3.) Demographic crisis (10 Billion population)
4.) Economic crisis (see your daily newspapers)

Will converge to a difficult future around 2050

Future is, what we make of it.

Investing in clean energy future will solve and ease all four crisis conditions simultaneously
THANK YOU FOR YOUR ATTENTION