Nanotechnology in Photovoltaics

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Our laboratory

Two lines of research on photovoltaic materials:

Thin film PV (CdS/CdTe-based)
Novel nanostructured materials – low-cost and high efficiency

Part of MEL, Laboratory for Energy Materials

research and services in the field of energy materials, including photovoltaic installations (e.g. 20 kW installation on DMRN's building roof, 20 kW installation on the City Hall's Roof in Trieste, ...)

Our laboratory

Doctoral student: Luca Cozzarini

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Emanuele Slejko Giulio Pipan Stefania Cacovich Luca Pavan

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Contents

Introduction – Why photovoltaics (PV)?

Evolution of PV (economical – technical – social)

Current PV technologies
Basic physics
Si-based technology
Thin films

Emerging technologies
High efficiency approaches (Tandem)
Low-cost approaches (Biomimetics)

Third generation technologies
Nanostructured materials – colloidal solids

Photovoltaics

Direct conversion of solar energy to electrical energy (for free!) Why Photovoltaics?

Growth of the Energy Demand

- Particularly in the developing countries-



Growth of the Energy Demand

- Particularly in the developing countries-







Earth at Night

Temperature rising (?)



http://www.globalwarmingart.com/wiki/Image:Carbon_Dioxide_400kyr_Rev_png



Ice Melting





Pasterze Glacier, Austria Change between 1875 and 2004

http://www.worldviewofglobalwarming.org/pages/glaciers.html



Earth at Night

Economic sanctions

la Repubblica.it

Ultimo aggiornamento lunedi 08.01.2007 ore 10.45

AMBIENTE

Entro gennaio convocati gli esperti che hanno preparato la ricerca per la Ue Nel conto i danni a turismo e agricoltura e le sanzioni per le violazioni di Kyoto

Clima, minaccia per l'economia l'Italia rischia decine di miliardi



Photovoltaics vs. other Renewable Resources



Evolution of Photovoltaics

- Economical
- Technical
- "Social" acceptance and integration

Economical Evolution: Photovoltaic Market

New Markets



Market size and growth

- World Market: € 15B
- Demand and supply growth: 35%/year
- Demand exceeds supply

Trends in photovoltaic applications, Survey report of selected IEA countries between 1992 and 2005, report IEA-PVPS T1-15:2006

DOE Solar Energy Technologies Program, Multi-Year Program Plan 2007-2011, U.S. Department of Energy, Energy Efficiency and Renewable Energy





Technological evolution

Technology evolution: Efficiency increase



NREL - US Dept.of Energy

Technology evolution: Efficiency increase



Tecno-Economical Evolution - Cost and Efficiency – PV Figures of Merit -



Integration of PV

Traditional Photovoltaic Installations



Integration: Aesthetics



Integration: Aesthetics



Integration: Aesthetics & Function



Integration: Aesthetics & Function



Current PV Technologies



Photovoltaic Effect



Photovoltaic Effect



p-n junction



Photovoltaic Effect


Photovoltaic Effect

Choice of materials



 Materials with good absorption of the solar radiation



- "Perfect materials" (large mean free paths for the carriers)
- Short carrier paths

Silicon technology



Silicon technology – Record performance



	Single crystal silicon	Polycrystalline
Cell Record	24.7%	20.3%
Module record	22.7%	15.3%
Commercial modules	15-18%	12-15

Silicon Technology



Silicon Technology - Summary

 Mature Technology (max efficiency > 80% thermodynamic limit)



Large quantities of pure silicon are needed
high cost of raw material

Limitation in raw material supply



Tecno-Economical Evolution - Cost and Efficiency – PV Figures of Merit -





Thin Film Solar Cells

Materials with:

- high absorption coefficient
- good match with the solar spectrum (1.5 eV)

- Less active material is needed (thin films: 0.1 – 10 um)
- Lower cost
- Less problems with supply of raw materials
- Short carrier paths (perfection requirements are relaxed)

Thin Film Solar Cells

Medium efficiency – Low Cost

	CdTe	CIGSS	Amorphous Si
Cell Record	16.5%	19.5%	9.5%
Module record	10.7%	13.4%	
Commercial modules	8-10%		4-7%



Technology evolution: Efficiency increase



Tecno-Economical Evolution - Cost and Efficiency – PV Figures of Merit -



Thin Film Solar Cells

- Young Technology(max efficiency is 30-40% of thermodynamic limit)
- •Films can be deposited on various substrates (flexible, architectural elements for building integration, etc.)
- •Low Cost
- Thermodynamic limit is still 30%
- Nanotechnology-based films are currently reaching the market

PV efficiency: Thermodynamic limit



PV efficiency: Thermodynamic limit





Max efficiency: 30%

Beyond The Single Junction Limit: Tandem cells



More efficient use of the solar spectrum

Tandem Cells



•Current efficiency record > 40%

- •Multijunction cells very expensive
- Aerospace applications or terrestrial concentration

Tecno-Economical Evolution - Cost and Efficiency – PV Figures of Merit -



Why nanotechnology?

- Morphological advantages (surface area)
- Phenomena that govern optoelectronic properties of materials occur at the nanoscale

 Phenomena at the nanoscale are governed by the laws of quantum mechanics
new opportunities for controlling material properties



Dye-sensitized solar cell (DSSC) – Grätzel cell



Photosynthesis

- Energy is absorbed by the *antenna* complexes
- Cascade of energy transfer between donors and acceptors embedded in antennas (FRET)
- Energy is funneled to the reaction center
- Subsequent multistep electron transfer
- This creates a charge-separated state which lasts for 10s of μ s or more, with a ~100% QE





- Absorption is only efficient at specific wavelenghts
- To reach the charge-separated state the electron needs to spend energy
- Energy converted in chemical energy ~ 9%



Artificial Photosynthesis: Basic Example



Artificial Photosynthesis Requirements

- Appropriate redox potentials and excitation energy for donors and acceptors (*quantum yield*)
- Small reorganization energy λ (- $\Delta G_{cs} \sim \lambda$ and - $\Delta G_{CR} >> \lambda$) to favor forward electron transfer (*charge separation time*)
 - •Distance between donors and acceptors
 - •Solvent characteristics
 - •Vibrational modes of the molecules

Artificial Photosynthesis: A more efficient scheme



H. Imahori et al., Adv. Func. Materials 14, 525 (2004)

Artificial Photosynthesis: Mimicking energy transfer



Artificial Photosynthesis on Transparent Conductive Oxide (ITO)



Artificial Photosynthesis: Hierarchical assembly for enhancing absorption



Artificial Photosynthesis: Hierarchical assembly for enhancing absorption





L. Forlov et al., Adv. Materials 17, 2434 (2005)

Beyond The Single Junction Limit: Tandem cells



More efficient use of the solar spectrum

Intermediate Band Materials Beyond single junction limits (at low cost!)



Making an Intermediate Band Material

Quantum dots embedded in a semiconductor

Nanotechnology at the service of PV



Photovoltaic Devices Based on Intermediate Band Materials

•Max efficiency 47%

atro

rc0

rato

strato p

PU

- •Current record for single-junction cell: 28.3%
- Scalable, low-cost production approaches
- Diversity of substrates excellent integration (nanoinks and photovoltaic "paints")

Tecno-Economical Evolution - Cost and Efficiency – PV Figures of Merit -





Beyond The Single Junction Limit: Other approaches

- Multiple carrier generation using high energy photons to extract more than one electron per photon
- Hot electron extraction

extracting high energy photogenerated electrons before they thermalize



Thermodynamic limiting efficiency (both cases): 86.8%

Properties of nanomaterials

Phenomena at the nanoscale are governed by the laws of quantum mechanics.

new opportunities for controlling material properties

Phenomena that govern optoelectronic properties of materials occur at the nanoscale
Properties of nanomaterials What does "nano" mean?

A material is "nano" when a selected property starts to differ from its bulk behavior



Electrons in a (spherical) box



- Electrons can be described by waves
- Confined waves can only have a discrete set of wavelengths
 - In confined systems, electrons can only assume discrete values of energy

Position of energy levels depends upon confinement (size of the box)

Quantum Dots "Artificial atoms"



As for atoms, quantum dots have discrete electron energy levels

Nanocrystals





Typical size: 1 - 100 nm ($10^2 - 10^5$ atoms) Most atoms are at the surface (75% for 1 nm nanocrystals) Essentially free of lattice defects

Nanocrystals



1415

35

Fig. 2.1. The percentage of surface atoms changes with the palladium cluster [C. Nützenadel, A. Züttel, D. Chartouni, G. Schmid, and L. Schlapbach, *Eur. P*_{17 Shells} 245 (2000).]

Semiconductor nanocrystals (quantum dots): Optical properties





Wavelength / nm

Quantum dot absorption and emission

Dependence on size





Semiconductor Nanocrystals: Synthesis

1	IA ¹ H ³ Li	IIA ⁴ Be	Periodic Table											0 He ¹⁰ Ne				
3	¹¹ Na	¹² Mg	IIIB	IVB	VB	VIB	VIIB		- VII -		IB	IIB	¹³ Al	¹⁴ Si	¹⁵ P	¹⁶ S	¹⁷ CI	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 	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 TI	82 Pb	83 Bi	⁸⁴ Po	85 At	⁸⁶ Rn
7	87 Fr	88 Ra	89 +Ac	¹⁰⁴ Rf	¹⁰⁵ Ha	¹⁰⁶ Sg	¹⁰⁷ Ns	¹⁰⁸ Hs	¹⁰⁹ Mt	110 110	111 111	¹¹² 112	113 113					
*	Lanth Series	anide s	58 Ce	⁵⁹ Pr	60 Nd	⁶¹ Pm	62 Sm	⁶³ Eu	Gd	65 Tb	66 Dy	67 Ho	⁶⁸ Er	⁶⁹ Tm	70 Yb	⁷¹ Lu		
+	Actini Series	de s	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	¹⁰⁰ Fm	¹⁰¹ Md	102 No	103 Lr		

Semiconductor Nanocrystals: Synthesis

Colloidal synthesis of cadmium selenide

Cd-oleate + Se-TOP

CdSe + products



Semiconductor Nanocrystals: Colloidal Synthesis



TIME, TEMPERATURE and CONCENTRATION control reaction kinetics Surfactant are needed to avoid cluster formation

Nucleation



$$R_N = nP\Gamma = \left\{\frac{C_o kT}{3\pi\lambda^3\eta}\right\} \exp\left(-\frac{\Delta G^*}{kT}\right)$$









Paul Alivisatos, UC Berkeley

Nanostructured materials – Colloidal solids

A chance to design novel materials with entirely new properties





Methods for assembling colloidal solids







Bio-templated nanomaterials



E. Hu, UCSB A. Belcher, MIT

Assembly and structural control



C.B. Murray et al., Annu. Rev. Mater. Sci 30, 545 (2000)

QD-solid assembly: QD Distance Engineering



Curve	Capping agent	Atoms per chain	Interparticle distance (Å)
h	Trihexadecylphosphate	16	17
i	Trioctylphosphine calchogenide	8	11
j	Tributylphosphine oxide	4	7

C.B. Murray et al., Science 270, 1335 (1995)



Y. Yin, A.P. Alivisatos, Nature **437**, 664 (2005)

Electronic properties of colloidal solids



QD-solid assembly: Bi-component QD-Solid





F.X. Redl et al., Nature 423, 968 (2003)

Materials engineering







CB

VB

Our approach for sinthesizing an IB material

Matrice di ZnSe matrix – CdSe QDs





NCs Growth Kinetics – Control of Size



Assembly: Control of interparticle forces





Assembly: Ordering



Uniform Thin Films of NC assemblies



Densification of NC assemblies



Optical properties of NC assemblies



Concluding Remarks

•PV is at a "tipping point" – breakthrough technology is just around the corner

•Bio- and Nanotechnology will likely be the key to high performance, low cost PV devices

 Colloidal routes to fabricate PV materials are extremely promising:

•The structure can be finely engineered at the nanoscale

•Cost can be reduced (ambient process conditions)

Aknowledgements

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State of the art

Table I. Confirmed terrestrial	cell and su	bmodule effi	ciencies at 25	s measured	unde	er the global AM	$M1.5$ spectrum (1000 Wm^{-2})
Classification*	Effic. [†] (%)	Area [‡] (cm ²)	V _{oc} (V)	J_{sc} (mA/cm ²)	FF [§] (%)	Test centre [∥] (and Date)	Description
Silicon							
Si (crystalline)	$24{\cdot}7\pm0{\cdot}5$	4.00 (da)	0.706	42.2	82.8	Sandia (3/99)	UNSW PERL ⁹
Si (multicrystalline)	$20{\cdot}3\pm0{\cdot}5$	1.002 (ap)	0.664	37.7	80.9	NREL (5/04)	FhG-ISE ¹⁰
Si (thin-film transfer)	16.6 ± 0.4	4.017 (ap)	0.645	32.8	78.2	FhG-ISE (7/01)	U. Stuttgart $(45 \mu m \text{ thick})^{11}$
Si (thin-film submodule)	9.8 ± 0.3	96·3 (ap)	0·487 [¶]	27·0 [¶]	74.5	Sandia (8/06)	CSG Solar $(1-2 \mu m \text{ on glass}; 20 \text{ cells})^5$
III–V Cells							
GaAs (crystalline)	$25{\cdot}1\pm0{\cdot}8$	3.91 (t)	1.022	28.2	87.1	NREL (3/90)	Kopin, AlGaAs window ¹²
GaAs (thin-film)	$24{\cdot}5\pm0{\cdot}5$	1.002 (t)	1.029	28.8	82.5	FhG-ISE (5/05)	Radboud U., NL ¹³
GaAs (multicrystalline)	$18 \cdot 2 \pm 0 \cdot 5$	4.011 (t)	0.994	23.0	79.7	NREL (11/95)	RTI, Ge substrate ¹⁴
InP (crystalline)	21.9 ± 0.7	4.02 (t)	0.878	29.3	85.4	NREL (4/90)	Spire, epitaxial ¹⁵
Thin-film chalcogenide							
CIGS (cell)	$18.8 \pm 0.5^{\#}$	0.998 (ap)	0.699	33.8	79 .4	NREL (2/06)	NREL, CIGS on glass ¹⁶
CIGS (submodule)	16.6 ± 0.4	16·0 (ap)	0.661 [¶]	33·4 [¶]	75.1	FhG-ISE (3/00)	U. Uppsala, 4 serial cells ¹⁷
CdTe (cell)	16.5 ± 0.5 [#]	1.032 (ap)	0.845	25.9	75.5	NREL (9/01)	NREL, mesa on glass ¹⁸
Amorphous/nanocrystalline Si							
Si (amorphous)**	9.5 ± 0.3	1.070 (ap)	0.859	17.5	63.0	NREL (4/03)	U. Neuchatel ¹⁹
Si (nanocrystalline)	$10{\cdot}1\pm0{\cdot}2$	1.199 (ap)	0.539	24.4	76.6	JQA (12/97)	Kaneka $(2 \mu m \text{ on glass})^{20}$
Photochemical							
Dye sensitised		1.004 (ap)	0.729	21.8	65.2	AIST (8/05)	Sharp ²¹
	10.4 ± 0.3						
Dye sensitised (submodule)	$6 \cdot 3 \pm 0 \cdot 2$	26.5 (ap)	6.145	1.70	60.4	AIST (8/05)	Sharp ²²
Organic							
Organic polymer ^{††}	$3 \cdot 0 \pm 0 \cdot 1$	1.001 (ap)	0.538	9.68	52.4	AIST (3/06)	Sharp, fullerene derivative ²³
Multijunction devices							
GaInP/GaAs/Ge	$32{\cdot}0\pm1{\cdot}5$	3.989 (t)	2.622	14.37	85.0	NREL (1/03)	Spectrolab (monolithic)
GaInP/GaAs	30.3	4.0 (t)	2.488	14.22	85.6	JQA (4/96)	Japan Energy (monolithic) ²⁴
GaAs/CIS (thin-film)	$25{\cdot}8\pm1{\cdot}3$	4.00 (t)	-	-	-	NREL (11/89)	Kopin/Boeing (4 terminal) ²⁵
a-Si/µc-Si (thin submodule) ^{‡‡}	11.7 ± 0.4	14·23 (ap)	5.462	2.99	71.3	AIST (9/04)	Kaneka (thin-film) ²⁶

Stato dell'arte

Table II. Confirmed terrestrial module efficiencies measured under the global AM1.5 spectrum (1000 W/m ²) at a cell temperature of 25°C										
Classification*	Effic. [†] (%)	Area [‡] (cm ²)	V _{oc} (V)	Isc (A)	FF [§] (%)	Test centre (and Date)	Description			
Si (crystalline) Si (multicrystalline) Si (thin-film polycrystalline) CIGSS CdTe a-Si/a-SiGe/a-SiGe (tandem)¶	$\begin{array}{c} 22.7 \pm 0.6 \\ 15.3 \pm 0.4^{\parallel} \\ 8.2 \pm 0.2 \\ 13.4 \pm 0.7 \\ 10.7 \pm 0.5 \\ 10.4 \pm 0.5 \end{array}$	778 (da) 1017 (ap) 661 (ap) 3459 (ap) 4874 (ap) 905 (ap)	5.60 14.6 25.0 31.2 26.21 4.353	3.93 1.36 0.318 2.16 3.205 3.285	80·3 78·6 68·0 68·9 62·3 66·0	Sandia (9/96) Sandia (10/94) Sandia (7/02) NREL (8/02) NREL (4/00) NREL (10/98)	UNSW/Gochermann ²⁷ Sandia/HEM ²⁸ Pacific Solar (1–2 µm on glass) ²⁹ Showa Shell (Cd free) ³⁰ BP Solarex ³¹ USSC (a-Si/a-Si/a-Si:Ge) ³²			

Moduli basati su film sottile



Esempi: Silicio amorfo; CIGS; CdTe

Moduli basati su film sottili di CdTe

- Proprietà elettroniche ideali
 (bandgap 1.5 eV massimo utilizzo della radiazione solare)
- Disponibilità delle materie prime
- Robustezza e varietà di processi produttivi disponibili
- Provata fattibilità industriale (First Solar; Antec)

Economia dell'industria fotovoltaica



1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010
Vendite First Solar



Costo dell'energia fotovoltaica



Altre applicazioni



Schermi piatti



Basso consumo Alta efficienza Un solo materiale per vari colori



La selezione della **dimensione dei nanocristalli** consente la **scelta del colore** da uno spettro continuo Applicazioni: Display più luminosi, con miglior riproduzione del colore, a basso consumo





Dyes biocompatibili



Studio del comportamento di cellule, ed in generale degli esseri

Diagnosi e cura dei tumori



Le nanoparticelle vengono funzionalizzate in modo da venir accumulate presso il tumore

Le proprietà di emissione vengono utilizzate per individuare il tumore

Le proprietà di assorbimento vengono utilizzate per eliminare il tumore



Considerable efforts are being directed toward developing multifunctional nanomedicines. Researchers from the Korea Advanced Institute of Science and Technology and Seoul National University have developed polymer nanoparticles (NPs) that act as multimodal imaging probes and use magnetic guidance to improve drug delivery [Kim *et al., Adv. Mater.* (2008) 20, 478].

The platform comprises four key components: (i) biodegradable poly(D,L-lactic-*co*-glycolic acid) (PLGA) NPs (100–200 nm in diameter) as the polymer matrix; (ii) hydrophobic, inorganic nanocrystals embedded into the matrix, either superparamagnetic Fe₃O₄ nanocrystals (15 nm diameter) for MRI contrast and magnetically guided drug delivery or CdSe/ZnS semiconductor quantum dots (3 nm in diameter) for optical imaging; (iii) the chemotherapeutic drug doxorubicin (DOXO) incorporated into the polymer matrix in NP form; and (iv) finally, cancer-targeting folate conjugated onto the modified PLGA NPs via polyethylene glycol (PEG) groups.

MRI and fluorescence imaging tests were performed on untreated cancer cells over-expressing folate receptors and cells mixed with either folate-free or folate-coated functionalized PLGA (containing Fe₃O₄ or CdSe/ZnS, as appropriate). Both techniques detected cancer cells treated with the NPs, with the best results achieved for folate-coated particles. When an external



Transmission electron micrographs of uncoated PLGA NPs containing the chemotherapeutic drug DOXO and superparamagnetic Fe₃O₄ nanocrystals. (Credit: Jaeyun Kim, Seoul National University.)

magnetic field is applied, the sensitivity of MRI to the cancer cells increases even further. Fluorescence observations confirm that CdSe/ZnS-impregnated NPs can deliver a chemotherapeutic payload into target cells. Confocal laser scanning microscopy and flow cytometry similarly confirm cellular uptake of the Fe₃O₄-containing NPs. As expected, uptake of these particles is improved when an external magnetic field is applied.

In vivo studies are now planned to test whether the fully functionalized NPs can, indeed, be used to image tumor volumes and target drug delivery in the presence of an external magnetic field. Taeghwan Hyeon of Seoul National University is optimistic. "We expect the NPs will accumulate at the tumor site, allowing the tumor to be detected and destroyed at the same time," he says. Paula Gould

Inchiostri a fluorescenza Sicurezza e tecnologie anti-contraffazione



Main Losses in PV Devices



Sommario

Tecnologia	Rendimento	Costo €/Wp	Tempo di ritorno dell'energia [anni]	Ritorno investimento energetico (EROI)	
Silicio monocristallo	15-22%	4-5	2-5	5-15	
Silicio policristallo	12-15%	4	1.7-3.5	8-17	
Film sottili	5-13%	2-3	1-1.5	17-30	
Celle tandem	30-42%	alto	?	?	
DSSC	5-10%	(2-3)			
Materiali organici	3-6%	(1-2)	<1	>50	
Nanomateriali	?	(<1)			

The bandgap dilemma





Absorption coefficients



Minimum thickness for full absorption



 $I = I_0 exp(-\alpha z)$



$$f(d) = \frac{\int_{0}^{\infty} (1 - \exp(-\alpha(\lambda)d)N_{ph}(\lambda)d\lambda)}{\int_{0}^{\lambda_{g}} N_{ph}(\lambda)d\lambda}$$

Minimum thickness for full absorption

Legge di Lambert – Beer $I = I_0 exp(-\alpha z)$



$$\int_{a}^{\infty} (1 - \exp(-\alpha(\lambda)d)N_{ph}(\lambda)d\lambda)$$
$$f(d) = \frac{0}{\lambda_{a}}$$

 $N_{ph}(\lambda)d\lambda$



