



2132-14

Winter College on Optics and Energy

8 - 19 February 2010

Organic/Inorganic hybrid solar cells

G. Gigli University of Salento Italy

Organic/Inorganic hybrid solar cells

Giuseppe Gigli National Nanotechnology Laboratory of CNR-INFM Innovation Engineering Dep., University of Salento Italian Institute of Technology (IIT)

Solar light

Anode

Organic/inorganic

hybrid material

Cathode

Glass

Contents

- New generation Solar cells
- Inorganic Semiconductor Nanocrystals
- Device structure, working mechanisms
- Some examples
- **Strategies for improving the performance**

Silicon Solar Cells



Well established and robust technology

Long life time (>20years)

Expensive technology (3-6€/Wp)

Silicon availability?





Amorphous film configuration

Power conversion effciency

Fable 1: Characteristics of the highest confirmed efficiencies for a range of photovoltaic cell technologies ^[2]									
Material System	J _{SC} [mA·cm ⁻²]	Voc [V]	Fill Factor	η [%]					
GaInP/GaAs/Ge	14.4	2.62	0.85	32					
GaAs (crystalline)	14.2	2.49	0.86	30					
Si (crystalline)	42.2	0.71	0.83	25					
InP (crystalline)	29.3	0.88	0.85	22					
Si (polycrystalline)	37.7	0.66	0.81	20					
CuInS ₂	8.4	2.64	0.75	18					
CdTe	25.9	0.85	0.76	17					
Si (nanocrystalline)	24.4	0.54	0.77	10					



Small molecular weight Solar cells (PCE ~5%)

Advantages:

Can Fabricate complex multilayer devices→ performances
Relatively easy to model
No need to make molecule soluble→performance
Materials can be purified at high degree prior to use

Disadvantages:

•Formation of thermodinamically stable phases is kinetically limited



Polymer-Acceptor Solar Cells (PCE ~5%)





Advantages:

Very low cost processing (roll to roll, screen printing, doctor blading, etc.)
Morphology control by solvent choice, drying time, etc

Disadvantages:

•Materials must be designed with solubility in mind (performances degrade)

Organic-Inorganic Hybrid Solar cells



Fabrication:

Prestructure inorganic phase using self assembly, templated growth, nanopatterning.
Fillin with polymer

•Advantages:

You can lock-in geometry and design polymer without worring about morphology→optimal ordered path for carrier collection, efficient exciton diffusion
Efficient polymer alignment→ mobility enhancement Modelling

Disadvantages:

•Hard to make precise nanostructures

Silicon Nanowire Radial p-n Junction Solar Cells



a low-temperature wafer-scale etching and thin film deposition method were demonstrated for fabricating silicon n-p core-shell nanowire solar cells. The devices showed efficiencies up to nearly **0.5%**.

J. AM. CHEM. SOC. 2008, 130, 9224-9225

Solid State Dye Sensitised (PCE ~4%)

Fabrication:

Dye on nanoporous inorganic acceptor. Hole conducting polymer replaces electrolyte



Advantages:

•High EA material $(TiO_2) \rightarrow$ better carrier separation

Disadvantages:

Thick devices needed → need high carrier mobility

Polymer-Inorganic Nanocrystal Solar cells

Fabrication:

•Blend of polimer (organic) with inorganic semiconducting nanocrystal

•Advantages:

Shape control over nanoparticles
Energy gap control
Can cover IR wavelength
Solution processing (cheap, flexible substrates)

Disadvantages:

Hard to control nanoscale morphologyHard to assure good Np-Np contact





Surface/Volume Ratio



Colloidal Nanocrystals

Surfactants control the size and shape of nanocrystals and allow their solubilization in organic solvents

CdSe/ZnS







Synthesis of Colloidal Nanocrystals



that is based on the high temperature reaction of molecular precursor in the presence of coordinating organic molecules as dynamic templates for nanocrystal growth.

Synthesis of Colloidal Nanocrystals



The Shape of Nanocrystals

CdSe Nanocrystals

Dots

Hyperbranched Same materials but different shapes Rods



Synthesis of Colloidal Nanocrystals

Seeded Growth Approach

Advantages:

- Different shape
- Different combination of material (Heterostructure)
- Narrow distribution of length and diameter

Separation of nucleation and growth

To HETEROSTRUCTURE



CdSe/CdS heterostructures Tem Image

CdSe/CdS Rods



Carbone et al. Nanoletters, 2007





Altered lattice parameters

New type II heterostructures

A type II colloidal heterostructure consists of semiconductor materials where both the valence and conduction Band in the core are lower (or Higher) than in the shell



Charge separation can occur at the interface between the two semiconductor materials

New type II heterostructures Tem Image

CdSe/CdTe



ZnTe/CdS



Optical Properties tuning



Size dependent band gap





Quantum Dots size



Shape dependent band gap



$$E_g(R) = E_g^b + \frac{\hbar^2 \pi^2}{2\mu R^2}$$

$$E_{l,n}^{e,h} = \frac{\hbar^2 \rho_{n,l}^2}{2m_{e,h}^* R^2}$$

Organic-inorganic semiconducting NCs Hybrid SCs



How an Hybrid Solar Cell Works





Charge

collection

IOA irradiance: amount of global horizontal radiation that a location would receive if there was no atmosphere or clouds. It resembles closely that of a black body at 5250°. SL irradiance: TOA attenuated by scattering from molecules, aereosol, dust particles as well as absorption .PV



 η_A = Photon Absorption Yield (optical absorption coeff and Thickness)



 η_{diff} = Exciton diffusion Yield poly

(ability of exciton to diffuse through the polymer without recombination (loss)



Process

collection



Probability that the hole and the electron will be separated by the internal electric field at the interface

Scanning Kelvin Force Microscopy (SKFM) on hybrid solar cells: P3HT-CdSe hyperbranched nanocrystal



Topography of P3HT-CdSe nanocrystals: 20⁻ it revelas nanocrystal aggregates of the electron 40⁻ acceptor (A; CdSe) embedded into a matrix of 60⁻ the electron donor (D; P3HT)

Light on





The Skfm technique allows the determination of the local surface potential of nanostructured materials in a non invasive way detecting the electrostatric-force interaction between the tip and the sample

Surface potential

The contrast enhancement demonstrates that photogenerated excitons are split at the interface between the two materials, leading to the accumulation of the electrons in CdSe nanocrystals and holes in the P3HT polymer matrix

Light off





Charge transport involves hopping processes and is affected by traps in the composite film. Traps originate from structural defects or impurity species, They provide localised energy minima of variable depth for charge transport which reduce mobility.

High mobilities minimise recombination losses, carriers are trasported to the electrodes more quickley

Carrier transport in bulk heterojunction structures



Interconnected with minimal aggregation



The external quantum efficiency EQE

It's defined as the number of the electrons flowing in the external circuit per photon incident on the PV cell.



Solar cell efficiency and its light power dependence



Ideal nanocrystal-polymer solar cells



How to improve efficiency of hybrid solar cells

some general rules for preparing efficient hybrid solar cells

- I. High electron and hole mobilities for NCs and polymers, respectively.
- II. High interfacial area of the bulk heterojunction structure.
- **III.** High extinction coefficients for NCs and polymers.
- IV. Optimum values of energy levels for NCs and polymers should be chosen so that they promote charge separation and transfer.
- V. Interpenetrating networks and good percolating paths.

Best results reported so far.....

Ma	Materials and performance parameters for a range of selected inorganic nanoparticle-polymer cells													
	Polymer ^a	NP ^b	$f_{\rm np}{}^{\rm c}$	$r_{\rm np}/{\rm nm}^{\rm d}$	$A_{\rm R}$	$A_{22}\!/10^{-20}~{\rm J}^{\rm e}$	Solvent	$A_{\rm eff}\!/\!\rm kT^{f}$	Thick/nm	EQE	$P/mW/cm^2$	$I_{sc}/mA/cm^2$	V _{oc} /V	PCE/%
1	OC_1C_{10} -PPV	CdSe tetpd	0.51	2.5	10	11.0	TCB	2.01	150	0.52	89	9.1	0.76	2.8
2	P3HT	CdSe nrods	0.65	2.5	13	11.0	TCB	2.01		0.70	92	8.79	0.62	2.6
3	APFO-3	CdSe nrods	0.51	2.5	10	11.0	Xylene	3.5	90	0.44	100	7.23	0.95	2.4
4	P3HT	CdSe hbrch		5.0	High	11.0					100	7.10	0.60	2.2
5	OC_1C_{10} -PPV	CdSe tetpd	0.51	2.5	10	11.0	CHCl ₃ /pyr	2.01	170	0.45	93	7.30	0.65	1.8
6	P3HT	CdSe nrods	0.65	3.5	8.6	11.0	CHCl ₃ /pyr	2.01	200	0.56	100	6.07	0.70	1.7
7	MDMO-PPV	ZnO	0.27	2.5	1	9.0	CBZ/MeOH	0.07	80	0.39	100	2.40	0.81	1.6
8	P3HT	CdSe nrods	0.43	3.5	4.3	11.0	CHCl ₃ /pyr	2.01			100	5.80	0.57	1.4
9	P3HT	CdSe hbrch	0.78	5.0	High	11.0	CHCl ₃ /pyr	2.01			100	3.35	0.62	1.15
10	MEH-PPV	CdSe tetpd	0.60	1.0	7	11.0	CHCl ₃ /pyr	2.01	100	0.46	80	2.86	0.69	1.13
11	MDMO-PPV	ZnO	0.15	3.0	1	9.0	CBZ/THF	0.07		0.26	90	2.30	1.14	1.1
12	P3HT	CdSe	0.62	2.5	1	11.0	CBZ/other	0.58	100		100	2.03	0.90	0.85
13	MEH-PPV	PbS		2.0	1	7.8	CBZ	0.003		0.21	5	0.13	1.00	0.70
14	APFO-3	ZnO	0.27	2.5	1	9.0	CBZ/CHCl ₃	0.07		0.24	100	3.10	0.51	0.45
15	P3HT	TiO_2	0.30	15	1	14.3	Xylene	6.7	100	0.15	100	2.76	0.44	0.42
16	P3HT	TiO ₂ -HgTe	0.25	2.3	1		CBZ		300	0.09	100	2.00	0.40	0.40
17	P3HT	ZnO-dye		40	9.4	9.0	CBZ	0.07	80	0.14	100	2.00	0.28	0.20
18	P3HT	CuInSe ₂	0.59	7.5	1.3		Toluene		200		80	0.30	1.00	0.15
19	P3HT	PbSe	0.37	3.0	1				60		100	1.08	0.35	0.14
20	MEH-PPV	CdSe tetpd		2.0	5	11.0	CHCl ₃ /pyr	2.01	100		80	0.02	0.33	0.003
21	MEH-PPV	PbS	0.34		1	7.8	CHCl ₃	0.36					0.33	0.001

Some examplesFrom Dots to hyperbranched NCs based solar cells....

Hybrid <u>Spherical NCs (Dots)</u>-Polymer SC





Rods naturally provide a direct path for electrical trasport. Long nanorods oriented in the Electric field (elctron trasport) direction can penetrate through a large portion of the device

Rod size can be adjusted to the device thickness required for optimal adsorption

In long NCs electron trasport is dominated by band conduction (in short NCs by hopping (traps).

Problem of solubility when length is increased

Hybrid <u>Nanorod</u>-Polymer SC

PCE=1.7%



Science, vol 295, 2425, 2002

CdSe nanorods and poly(3-hexylthiophene) based SC

Towards the ideal structure

organics



The efficiency of P3HT/CdSe nanorods can be improved by using a high boiling point solvent TCB for film deposition. The increased drying time allows larger-scale self-organized features to form in the P3HT, improving hole transport within the device. PCE is **2.6%**.



Phys. Chem. Chem. Phys., 2006, 8, 3557 - 3560



J. Phys. Chem. B 2006, 110, 25543-25546





Morphology control

•Possible sequential deposition, control of polymer thickness

Hybrid Hyperbranched NCs-Polymer SC





Nano Lett., 7 (2), 409 -414, 2007.

Reduced Problems of morphology control (usually stronlgy dependent on solvents, process condition (defects)on transport



Each hyperbranced NC span the entire device thickness thus contain a built in percolation pathway for trasport of electrons to the anode (cells in parallel)



Hyperbranched



45

type II tetrapods CdSe@CdTe using buffer layer



a, An energy diagram valence and conduction band levels for of type II tetrapods CdSe@CdTe, facilitating charge separation of electron and holes in CdSe cores and CdTe arms, respectively. b, Schematic drawing of the photovoltaic device structure based on CdSe@CdTe tetrapods



a, Current-voltage characteristics for PV cells with structure ITO/PEDOT-PSS/CdSe@CdTe/AI. b, Current-voltage characteristics for PV cells with structure ITO/PEDOT-PSS/CdSe@CdTe/C60/AI under illumination of one-sun AM 1.5G and in dark condition.



All-Inorganic Nanocrystal Solar Cells

By spin casting a bilayer and intimately mixed blends of CdTe-CdSe NCs. The devices are stable in air (no photo degradation processes), and post-fabrication processing allows for PCE approaching **3%**.



substrate



ITO

h

CdTe

No free carriers without illumination. Carrier extraction is driven not by means of a built in field created from a deplation region between pand n doped material, but by direct diffusion as dictated by type II D-A heterojunction.

free carrier thanks to interface and high rods aspect ratio (small confinement along long side) . Annealing to eliminate traps

Methods for improving performances of NCs based Solar Cells

- 1. Materials improvement
 - 1.1 Nanocrystals Optimization1.2 polymers with functional groups1.3 nanocomposites design
- 2. New techniques
 - 2.1 Self-organization and controlled assembly
 2.2 lithography technique--control exciton diffusion length and surface
 2.3 singlet-triplet exciton conversion
 2.4 Air-stable solar cell
 2.5 tandem solar cell

.....1.1 nanocrystals optimization

Harvest of near Infrared light in PbSe-polymer HSC



50

Improved Absorption

•Cadmium free- Material (no n-toxic)

Applied physics letters, 88, 183111, 2006, PCE is 0.14%

.....1.1 nanocrystals optimization

b. Novel CdTe-CdSe semiconductor nanocrystal heterostructures



Dumbbell structures

JACS communications 128,12590,2006. J. Phys. Chem. C, 111, 6538, 2007, single component PCE is 0.003%, Hybrid device PCE is 0.16%.

.....1.1 nanocrystals optimization

C. Nanocrystals networks



Nanotechnology, 17, 706, 2006,

----1.2 polymers with functional groups

Employing End-Functional Polythiophene To Control the Morphology of Nanocrystal-Polymer Composites in Hybrid Solar Cells



JACS communications 126, 6550, 2004, PCE is around 1.6%.



Electroactive surfactant---good charge separation and charge transfer
 Optimized size and shape of nano particles---good electron transport properties
 Ideal nanocomposites---with electroactive surfactant and networks

In order to have ideal nanocomposits,

1. Synthesis of electroactive surfactant

- the head groups must have high affinity for Ncs, like phosphonic acid group
- the end groups must provide solubility in a chosen solvent, like alkyl substituents



- 2. Synthesis of size and shape controlled Ncs
- 3. Ligand exchange to displace TOPO and create desired NCs-surfactant complexes
- 4. Create networks

2. New techniques

-----2.1 Self-organization and controlled assembly

a. Self-Organization of Nanocrystals in Polymer Brushes.



b. Controlled assembly of hybrid bulk-heterojunction solar cells

Process, **ITO cleaning** Linker growing Ncs assembly **Polymer spincasting Evaporation (AI)**

ITO



J. Phys. Chem. B 110, 25543, 2006, PCE is still low 1%.





Because the two cells are in series, V_{oc} is increased to the sum of the individual cells.

The front single cell shows, $V_{OC}=0.66V$ $J_{SC}=9.2mAcm-2$ FF=0.50 PCE=3.0% The back single cell shows, <u>V_{OC}=0.63V</u> J_{SC}=10.8mAcm-2 FF=0.69 PCE=4.7%

The tandem cell shows, $\underline{V_{OC}}=1.24V$ $J_{SC}=7.8mAcm-2$ FF=0.67 PCE=6.5%

Science, Vol 317,222, 2007

2. New techniques

----2.4 Air-stable solar cell



The TiOx layer,

Acts as a good electron transport layer,

prevents the intrusion of oxygen and humidity into the polymers,

-----improving the lifetime of unpackaged devices exposed to air by nearly two orders of magnitude.

By introducing a titanium oxide (TiO*x*) layer, devices show excellent air stability and enhanced performance. *Adv. Mater.* 19, 2445, 2007

2. New techniques

-----2.3 singlet-triplet exciton conversion



FIG. 3. Dark and photovoltaic responses of hybrid solar cells made from P3HT/CdSe with and without Ir(mppy)₃, showing 100% increase in short-circuit current upon doping of Ir(mppy)₃.

Hybrid solar cells made of P3HT/CdSe With the addition of Ir complex were fabricated, and great enhancement in their photovoltaic response was observed.

---Appl. Phys. Lett. 90, 133509, 2007

The exciton diffusion length depends on exciton mobility and lifetime
Upon blending triplet metal complex with polymers, the intersystem corssing (ISC) rate in polymer can be greatly enhanced and the triplet exciton population would increase a lot, leading to a greating improved PV response.

Future work--- we can work on such system.

Why Hybrid Organics-Inorganic Nanocrystals Solar Cell?

Combine advantages of inorganic material, such as stability, with advantages of organics, such as cheap fabrication technology....