

## Nanomodules - Solar Energy Harvesting Devices

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Accepted 05 November 2013, Available online 01 December 2013, Vol.3, No.5 (December 2013)

### Abstract

Solar energy conversion have been used since beginning of lifecycle and is necessary vital for all living organism. A major technological need for harnessing solar energy is the transition from non-renewable fossil-fuel based energy economy to sustainable (renewable) energy one. Today's solar power technologies has little chance to compete with fossil fuels or large electrical grids and are too expensive for manufacturing large scale generation of electricity. Nanotechnology has already shown huge breakthroughs in solar energy conversion and provides methods for fabrication and use of structures and systems with size corresponding to the wavelength of visible light. The fascinating optical properties of nanoengineered materials made them suitable for future solar material and might be able to increase the efficiency of solar cells by facilitating photon absorption, multiple exciton generation, and electron collection, but the most promising application of nanotechnology is the reduction in manufacturing cost. Also utilizing nanotechnology in inexpensive solar cell would help to preserve the environment. This review is seeking to introduce This review is seeking to introduce nanotechnology based current solar cell technologies.

**Keywords:** Nanotechnology, Multiple exciton generation, Dye-sensitized solar cell, Quantum Dots, CNTs.

### 1. Introduction

"When we look at a prioritized list of the top 10 problems, with energy at the top, we can see how energy is the key to solving all of the rest of the problems from water to population." - R. Smalley. Energy supply has arguably become one of the most important problems facing humanity. The exponential demand for energy is evidenced by dwindling fossil fuel supplies and record-high oil and gas prices due to global population growth and economic development. This energy shortage has significant implications to the future of our society, for example, in order for 10 billion people to sustain their current lifestyle with their current energy consumption, we need a minimum of ten additional terawatts (TWs), an equivalent of 150 millions of barrels of oil per day (150 M BOE/Day), until the year 2050. The energy crisis is further exacerbated by major concerns about global warming from greenhouse gas emissions due to increasing fossil fuel consumption. At this large scale, solar energy seems to be the most viable choice to meet our clean energy demand. The sun continuously delivers to the earth 120,000 TW of energy, which dramatically exceeds our current rate of energy needs (13 TW). This implies that covering only 0.1% of the earth's surface with solar cells of 10% efficiency would satisfy our current energy needs; however, the energy currently produced from sunlight

remains less than 0.1% of the global energy demand. The major barrier for the large-scale use of solar energy is the high cost and inadequate efficiencies of existing solar cells. Innovations are needed to harvest incident solar photons with greater efficiency and economic viability (R. Smalley *et al.* 2005).

Solar electricity is a steadily growing energy technology today and solar cells have found markets in variety of applications ranging from consumer electronics and small scale distributed power systems to centralized megawatt scale power plants. Direct utilization of solar radiation to produce electricity is close to an ideal way to utilize the nature's renewable energy flow. The best commercial solar cells based on single crystal silicon are about 18% efficient. These conventional p-n junction cells, so-called first generation devices, suffer from the high cost of manufacturing and installation (C. Keeling *et al.*, T. Whorf *et al.* 1995). The second-generation devices consisting of CuInGaSe<sub>2</sub> (CIGS) polycrystalline semiconductor thin films can reduce the price significantly, but it does not reduce the challenge to make their efficiencies more practical. Now the third-generation solar cells, such as dye-sensitized solar cells (DSSCs), bulk heterojunction cells, and organic cells, are promising for inexpensive and large-scale solar energy conversion (N. Lewis *et al.*, G. Crabtree *et al.*, 2005).

The wide introduction of solar powered devices made from nanomaterials has the potential to revolutionize global economic development. Nanotechnology has ass-

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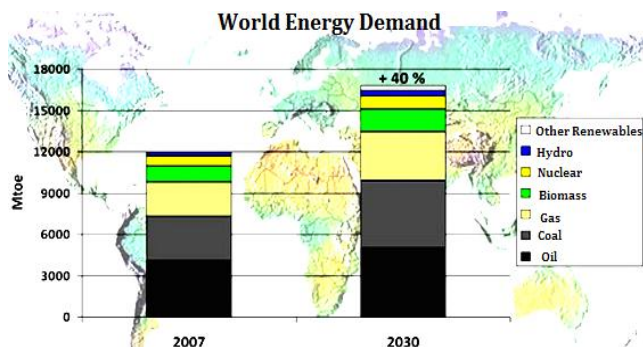


Figure 1 Global scenario on world energy demands

-umed a special status in semiconductor materials and catalysts. These two classes of materials could be considered as the key for solar energy conversion. Photocatalysts are a big family of nanomaterials (semiconductors/transition metal oxides) mostly applied in water treatment and solar water splitting for hydrogen production, among other useful applications; nanomaterials possess certain desirable properties like high catalytic activity, better stability in aqueous media, comparatively easier preparation techniques, and material economy (M. Zukalova *et al.* 2005). Chemists at the University of California, Berkeley, have discovered a way to make cheap plastic solar cells that could be painted on almost any surface. These new plastic solar cells utilize tiny nanorods dispersed within a polymer. The nanorods when absorb light of a specific wavelength they generate electrons. These electrons flow through the nanorods until they reach the aluminium electrode where they are combined to form a current and are used as electricity (NRM report 2005). Konarka Technologies is also pursuing the use of nanotechnology to improve solar energy. In fact, they are already manufacturing a product called, "Power Plastic" which absorbs both sunlight and indoor light and converts it into electricity. For patent reasons, their technology is kept secret, but the basic concept is that Power Plastic is made using nanoscale titanium dioxide particles coated in photovoltaic dyes, which generate electricity when they absorb light.

2. Significance of Nanomaterials in Solar cell

Nanoengineered materials contain structures with dimensions in the nanometer length scale such as polycrystalline materials with nanometer sized crystallites. The motivation for using nanostructured materials in solar cell emerges from the specific physical and chemical properties of nanostructures. The inclusion of nanoscale components in Photovoltaic would enhance the overall performance of solar cell mainly in two ways; first, the ability to control the energy bandgap provides flexibility and inter-changeability and second is; nanostructured materials enhance the effective optical path and significantly decrease the probability of charge recombination.

The size dependent properties of nanomaterials occurs mainly large surface area to volume ratio, means much more atoms are present on the surface of nanomaterials

than its bulk counterpart which make it more reactive and properties of materials get affected by atoms itself. The optical properties of certain material would change in a novel way. Surface plasmon resonance in metals and blue shifting in semiconductor dot are induces as a result of successive confinement of materials in nanometer range. The band gap energy of such optically active materials can be tuned with the irradiating radiation wavelength and are leading materials for nano solar cell technology with assumption that, these materials can enhanced the efficiency of solar cell up to 60% theoretically (E. Roduner *et al.*, 2010).

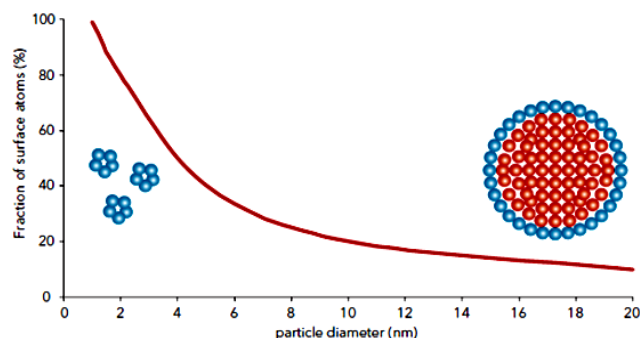


Figure 2 Fraction of atoms on nanomaterial surface

Multiple exciton generation (MEG), also called carrier multiplication is one more interesting phenomena of nanomaterials, involves in generation of multiple electron-hole pairs from the absorption of a single photon. In 2004, Schaller *et al.* and Klimov *et al.* demonstrated for the first time that multiple exciton generation occurred with very high efficiency in semiconductor nanocrystals.

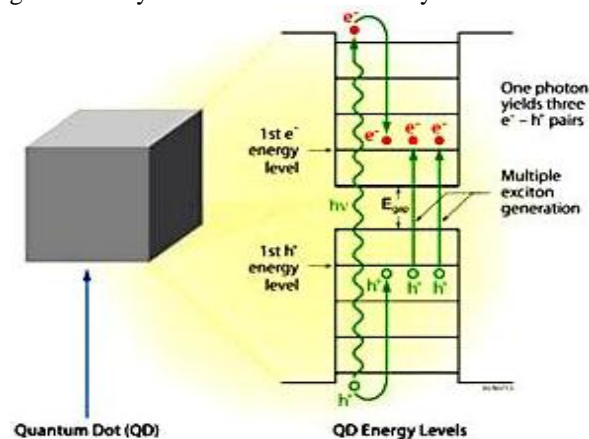


Figure 3 Multiple exciton generation in semiconductor crystal

MEG effect has been confirmed in semiconductor nanostructures (quantum dots) including PbSe, PbS, PbTe, CdS, CdSe, Si, InAs, and so on. Recently, under normal circumstances, the semiconductor materials can only produce a single exciton after absorbing a photon, and the high excitation energy photon wasted by phonon emission. If a photon can generate multiple excitons, the energy conversion efficiency of nanocrystal based solar cells may be improved significantly. MEG may considerably

increase the energy conversion efficiency of nanocrystal based solar cells (Schaller *et al.*, Klimov *et al.*, 2006). The quantum mechanical origin of MEG is still under debate and several possibilities have been suggested. Among the most credible explanations of the mechanism is considered to be impact ionization. Most experts focus their research activities in a few areas with the most prominent being thin films followed by polymer-based and hybrid cells. Some specific activities include improving efficiency of organic polymeric solar cells; bulk hetero-junction by electro-polymerization; using nanostructured materials in 3D configuration; light trapping nanostructured polymers; ion conducting polymers, passivation and barrier layers for organic solar cells; and improving the efficiency of conjugated polymer cells.

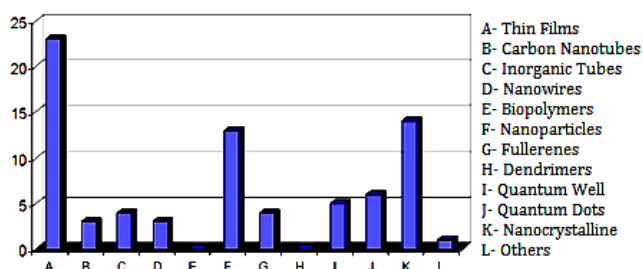


Figure 4 Expectation from nanomaterials

### 3. Dye-sensitized nanostructured solar cells (DSSC)

There are other systems besides semiconductors which can absorb visible light and store the acquired energy. Photosynthesis, based on chlorophyll is the primary energy source of the biosphere, so organometallic porphyrins are another possible way for solar energy conversion. It is also known (Moser *et al.*, 1887) that dyes can enhance the photoelectrochemical performance of semiconductors. Essentially the same process was developed at the same time for photography-panchromatic films and ultimately color photography.

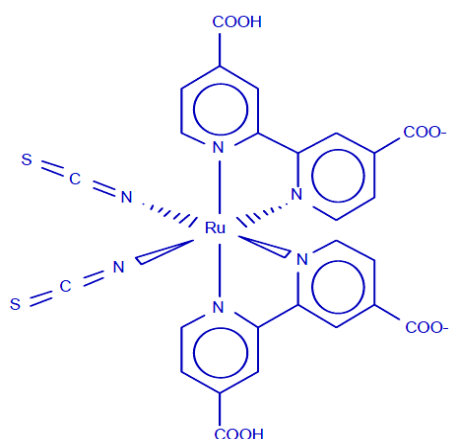


Figure 5 Standard N3 dye for photo electrochemical cell development-dithiocyanato bis (4, 4'-dicarboxylic acid-2, 2'-bipyridine) ruthenium (II)

Historically the dye-sensitization dates back to the 19<sup>th</sup> century, when photography was invented. The work of

Vogel in Berlin after 1873 can be considered the first significant study of dye-sensitization of semiconductors, where silver halide emulsions were sensitized by dyes to produce black and white photographic films (McEvoy *et al.*, Grätzel *et al.*, 1994). However the use of dye-sensitization in photovoltaics remained unsuccessful until a breakthrough at the early 1990's in the Laboratory of Photonics and Interfaces in the EPFL Switzerland. By the successful combination of nanostructured electrodes and efficient charge injection dyes, professor Grätzel and his co-workers developed a solar cell with energy conversion efficiency exceeding 7% in 1991 (O'Regan *et al.*, Grätzel *et al.*, 1991) and 10% in 1993 (Nazeeruddin *et al.*, 1997). This solar cell is called the dye-sensitized nanostructured solar cell or the Grätzel cell after its inventor. In contrast to the all-solid conventional semiconductor solar cells, the dye-sensitized solar cell is a photoelectrochemical solar cell i.e. it uses a liquid electrolyte or other ion-conducting phase as a charge transport medium. Due to the high efficiencies and good long-term stability reported for the dye-sensitized solar cells, the research interest in this technology grew rapidly during the 1990's.

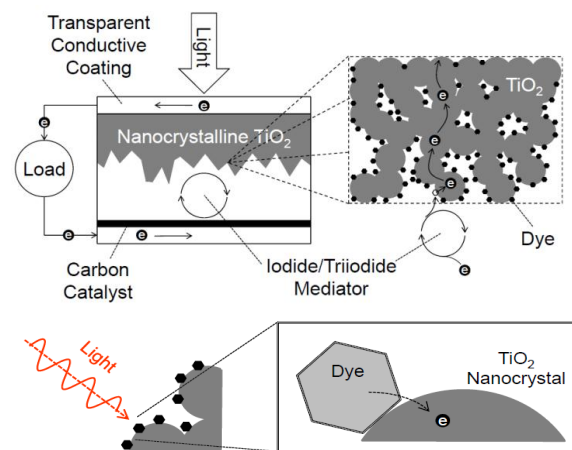


Figure 6 Dye-sensitized cell configuration and electron transfer mechanism

Working principle of DSSC is: (1) The incident photon is absorbed by the dye molecule adsorbed on the surface of nanocrystalline  $\text{TiO}_2$  particles and an electron from the molecular ground state  $S^0$  is excited to an excited state  $S^*$ , (2) The excited electron of the dye is injected into the conduction band of the  $\text{TiO}_2$  particles, leaving the dye molecule to an oxidized state  $S^+$ , (3) The injected electron percolates through the porous nanocrystalline structure to the transparent conducting oxide (TCO) layer of the glass substrate (negative electrode or anode) and finally through an external load to the counter electrode (positive electrode or cathode), (4) At the counter electrode, the electron is transferred to the triiodide in electrolyte to yield iodide, (5) The cycle is closed through reducing the oxidized dye by the iodide in the electrolyte. However, there is no net chemistry in terms of chemicals created or destroyed in the device, so the cell is regenerative (O'Regan *et al.*, Grätzel *et al.*, 1991).



The absorption of light in the DSSC occurs by dye molecules and the charge separation take place by electron injection from the dye to the  $\text{TiO}_2$  at the semiconductor electrolyte interface. A single layer of dye molecules however, can absorb only less than one percent of the incoming light and also, only the dye molecules in direct contact to the semiconductor electrode surface can separate charges and contribute to the current generation. A solution to this problem, developed by the Grätzel group, was to use a porous nanocrystalline  $\text{TiO}_2$  electrode structure in order to increase the internal surface area of the electrode to allow large enough amount of dye to be contacted at the same time by the  $\text{TiO}_2$  electrode and the electrolyte. Having this construction, a  $\text{TiO}_2$  electrode typically 10 mm thick, with an average particle (as well as pore) size typically in the order of 20 nm, has an internal surface area thousands of times greater than the geometrical (flat plate) area of the electrode, (O'Regan *et al.*, Grätzel *et al.*, 1991).

#### 4. Quantum Dot Solar Cell

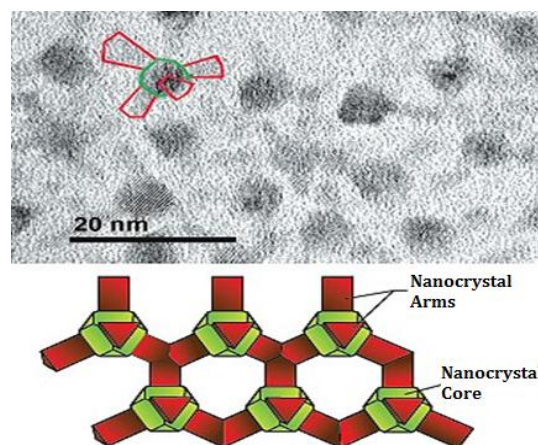
Quantum dots are zero dimensional nanocrystals usually made by direct bandgap semiconductors, with unique photochemical and photophysical properties that are not available from either isolated molecules or bulk solids, that are advantageous for the development of novel chemical and biosensors, as well as key of future electronics (QD LED, digital display, etc.). In comparison with organic dyes and fluorescent materials, QDs are emerging as a new class of fluorescent labels with improved brightness, resistance against photo bleaching and multicolor fluorescence emission (E. Pink *et al.*, Huang *et al.*, 2006). Researchers in recent years have focused on the advancement of photovoltaic conversion efficiency in third generation PV cells using QDs, formed into an order of 3-D array for strong electronic coupling between QDs so that excitons (electron and hole pair) will have a longer life for collecting and transporting 'hot carriers' to generate electricity at higher voltage (Schaller *et al.*, Klimov *et al.*, 2006). A photon makes it possible to generate multiple excitons (an average number of three excitons per photon absorbed) when the energy of the photon absorbed is far greater than the semiconductor bandgap. A. Nozik *et al.* (2001) and his team at NREL have measured the quantum yield of the multiple exciton generation (MEG) process in QDs of the lead-salt semiconductor family (PdSe, PbTe, and PbS). Very high quantum yields (up to 300 %) for charge carrier from MEG have been measured in all of the Pb-VI (VI = S, Se, Te) QDs.



**Figure 7** Size dependent multicolor emission of Quantum Dots

Researchers at Cavendish Laboratory in Cambridge, UK, have demonstrated that a tetrapod quantum-dot design improves charge transport. A tetrapod consists of a core and four arms, which can be tuned in length and diameter. Researchers at Rice University in Houston, Texas, USA, have also developed a method of synthesizing tetrapod shaped quantum dots with high selectivity and uniformity at low cost. The tetrapod shape for cadmium selenide quantum dots is achieved when their synthesis is carried out in the presence of cetyltrimethyl ammonium bromide. Solterra Inc. has licensed Rice University's fabrication technology and is now scaling up production of the cadmium selenide tetrapod quantum dots through continuous microreactor technology to levels that support the production of solar cells with a rated cell output of greater than 1 GW. By using tetrapod quantum dots in a polymer matrix, Solterra has demonstrated power conversion efficiencies of 6% from prototype cells with widths of ~0.1 m.

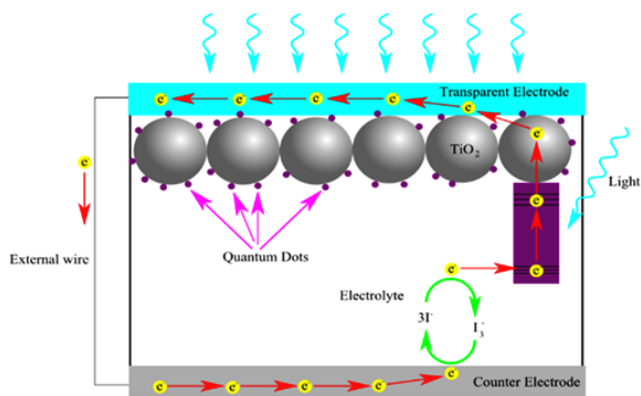
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**Figure 8** Armed Quantum Dots (tetrapods)

Quantum dots hold promise for low-cost solar cells because they can be made using simple, inexpensive chemical reactions. Scientists have calculated that quantum dots could be used to make thin-film photovoltaic's that are at least as efficient as conventional silicon cells, and possibly more efficient. The higher possible efficiency is because nanocrystals made of certain semiconductors can emit more than one electron for every photon absorbed. Plus, tweaking their size and shape changes the colors of light they absorb. The quantum dot band gap is tunable and can be used to create intermediate band gaps. The maximum theoretical efficiency of the solar cell is as high as 63.2% with this method (A. Nozik *et al.* 2001). Quantum dots would generate multiple exciton (electron-hole pairs) after collision with one photon.

In general this type of solar cell works on a principle, when a photon of light traveling into the cell and striking a quantum dot particle which in turn raises the energy of some of the electrons in the quantum dots. These excited electrons get injected into the titanium dioxide and travel through it to the conducting surface of the electrode.

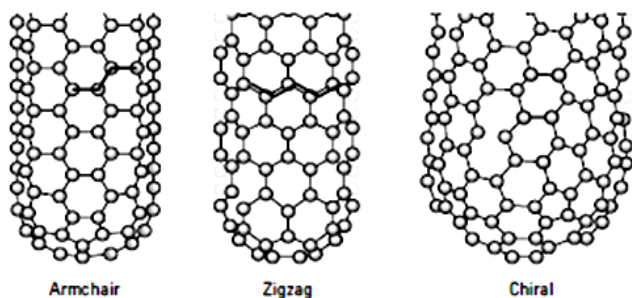


**Figure 9** Qdots solar cell configuration

While the electrons are traveling to the conducting surface of the electrode they leave holes in the quantum dots that need to be filled by other electrons. To fill these holes the quantum dots take electrons from the electrolyte. The electron depleted electrolyte in turn takes electrons from the counter electrode. This process creates a voltage across the cell and induces a current. Successful PV effects in such cells have been reported for several semiconductor QDs including InP, CdSe, CdS, and PbS (R. Gordon *et al.*, 2000). Recently, photovoltaic effects have been reported in structures consisting of QDs forming junctions with organic semiconductor polymers. In one configuration, a disordered array of CdSe QDs is formed in a hole-conducting polymer - MEH-PPV (poly (2-methoxy, 5-(2-ethyl)-hexyloxy-p-phenylenevinylene) (N. Greenham *et al.*, 1997). This allows a wider range of wavelengths to be absorbed and thus more electron-hole pairs to be generated. After electron-hole separation, the electrons are transported by the quantum dots to one electrode while the holes are transported by the polymer to the other.

**5. Carbon Nano Tubes (CNTs) Solar cell**

Carbon nanotubes are molecular-scale tubes, consisting of a hexagonal lattice carbon with remarkable mechanical and electronic properties. The structure of a nanotube can be represented by a vector, (n-row, m column), which defines how the graphene sheet is rolled-up. Nanotubes

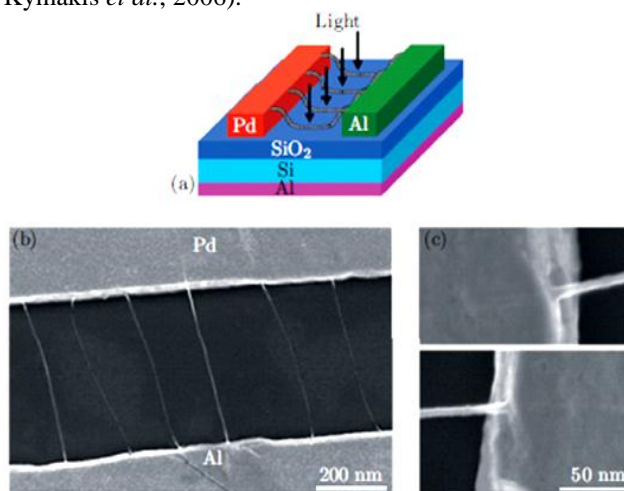


**Figure 10** Structural configuration of Carbon nanotube

can be either metallic or semiconducting depending on their structures. There are two types of nanotubes, the single walled carbon nanotubes (SWNTs) and the multi-

walled carbon nanotubes (MWNTs). SWNTs consist of a single graphite sheet wrapped into a cylindrical tube and MWNTs comprise an array of concentric cylinders (E. Kymakis *et al.*, 2003).

In PV cells technology, the nanometer-scale tubes, coated by the special p-type and n-type semiconductor (p/n) junction materials can be used to generate electrical current, which would increase the surface area available to produce electricity (E. Kymakis *et al.*, 2003). In recent years, nanotubes are used as the transparent electrode for efficient, flexible polymer-solar cells. In order to improve efficiency and reduce cost, a molecular dispersed heterojunction solar cell, consisting of a poly (3-octylthiophene), and dye (naphthalocyanine, i.e., NaPc) coated single-walled carbon nanotubes blend sandwiched between electrodes (aluminum and indium tin oxide (ITO) glass) was fabricated (B. Pradhan *et al.*, 2006). The dye (NaPc) acts as the sensitizer, which transforms electrons to the nanotubes and holes to the polymer. The nanotubes provide high field at the polymer/ tube interfaces for exciton dissociation. With the NaPc dye-sensitized nanotubes, the absorbance of the active layer in ultra-violet and red regions is significantly increased, resulting in much higher short circuit current. However, the open circuit voltage of the sensitized device is reduced by 0.2 V than the non-sensitized one. A SWCNT is an ideal channel for collecting and transporting charges across light-harvesting assemblies. Significant progress has been achieved in synthesizing semiconductor-CNT composite films in recent years. These earlier studies have mainly focused on establishing synthetic strategies and characterizing the composite systems, including CNTs with TiO<sub>2</sub>, SnO<sub>2</sub>, CdSe, and CdS nanocrystals (E. Kymakis *et al.*, 2006).

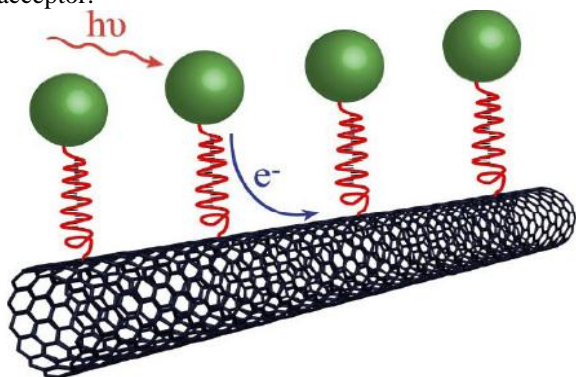


**Figure 11** Structure of the SWNT PV microcells. (a) Schematic diagram of SWNT PV cells. (b) SEM image of SWNT bundle array bridging the Pd and Al electrodes. (c) SEM images of the SWNT bundle ends nanowelded onto the metal electrodes

Most of the wet chemistry strategies involve in chemical functionalization of the CNT surface followed by the assembly of nanocrystals onto the CNTs via covalent,

noncovalent, or electrostatic interactions (E. Kymakis *et al.*, 2006). In 2008, C. Chen *et al.* from Shanghai Jiaotong University fabricated SWNT PV solar micro-cells. In this cell, a directed array of monolayer SWNTs was nanowelded onto two asymmetrical metal electrodes with high and low work functions, respectively, resulting in a strong built-in electric field in SWNTs for efficient separation of photogenerated electron-hole pairs. Under solar illumination, the power conversion efficiency can reach 12.6% (C. Chen *et al.*, 2008).

In addition, J. Choi *et al.* & A. Benjamin *et al.* (2010) reported a novel concept for harvesting solar energy by mimetic the nature concept of photo-conversion. In this approach biomolecules such as oligonucleotides (short strand RNA/DNA sequences) and carbon nanotubes were incorporated into self-assembling nanostructures and form the basis for a new class of nature-inspired electrochemical solar cells. Self-assembly, specific molecular recognition, and high affinity due to  $sp^2$  lattice of carbon nanotubes with oligonucleotides makes excellent hybrid elements. The oligomers are used as the glue in the self-assembly of donor chromophores (sensitizing dye) with CNTs. The structure of the sequence is designed to have strong target binding affinity with donor molecules, typically porphyrin derivatives, placing them in close vicinity for charge transfer into the nanotube acceptor.



**Figure 12** Schematic of nanohybrid oligonucleotides mediate interactions with carbon-nanotube acceptor.

In these nanohybrids, strong electron-transfer interactions are seen from the photo-excited electron donors to the carbon nanotubes. In the presence of nanotubes, photo-excited electrons in the conduction band transfer into the carbon nanotube's conduction band rather than fluorescing back to the valence band. As a result, the fluorescence signatures of donor samples are strongly quenched with increasing presence of carbon nanotubes. Over 90% of the donor fluorescence is quenched, freeing these electrons for harvesting solar energy (J. Choi *et al.*, A. Benjamin *et al.*, 2010).

## Conclusion

The sun provides enormous potential in helping to resolve the growing demand for energy worldwide; however, the high costs of implementing solar energy is a significant barrier compared with traditional energy sources, such as

fossil fuels. The cost of a photovoltaic system is directly related to the low conversion efficiency, diluted energy density of solar radiation, and costly materials and fabrication process. During the past decade, the development of nanoscience and nanotechnology has launched new ways to design efficient solar cells. Strategies have been developed to design nanostructure architectures of semiconductors, metals, and polymers for solar cells. Theoretical and modeling studies have also helped to understand the optical and electrical processes of the photovoltaic conversion. It may be expected that nano engineered solar cell would bring: (1) Inexpensive solar cells, which would utilize nanotechnology, would help to preserve the environment. (2) Coating existing roofing materials with its plastic photovoltaic cells which are inexpensive enough to cover a home's entire roof with solar cells, then enough energy could be captured to power almost the entire house. If many houses did this then our dependence on the electric grid (fossil fuels) would decrease and help to reduce pollution. (3) Inexpensive solar cells would also help to provide electricity for rural areas or third world countries. Since the electricity demand in these areas is not high, and the areas are so distantly spaced out, it is not practical to connect them to an electrical grid. However, this is an ideal situation for solar energy. (4) Cheap solar cell could be used for lighting, hot water, medical devices, and even cooking. It would greatly improve the standard of living for millions, possibly even billions of people. (5) Flexible, roller-processed solar cells have the potential to turn the sun's power into a clean, green, convenient source of energy even though the efficiency of Plastic photovoltaic solar cell is not very great, but covering cars with Plastic photovoltaic solar cells or making solar cell windows could be generate the power and save the fuels and also help to reduce the emission of carbon gases.

New generation of photovoltaic cells offers many opportunities; it also presents challenges such as in the following directions (1) ordered assemblies of two or more nano components on electrode surfaces; (2) new sensitizers or semiconductor systems that can harvest infrared photons; and (3) multiple exciton generation in semiconductor QDs. Worldwide, solar power is the star attraction for venture capitalists due to its booming laboratory research and commercialization. Although other forms of renewable energy can make significant contributions to current markets, sunlight is most available in the amount required to substitute completely for the energy quantities currently derived from hydrocarbons. In conclusion nanotechnology opens the new way for harvesting solar energy with its novel materials and sophisticated tools, and would transform the entire solar industry in terms of higher efficiency and cheap production of solar cells.

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