Review Article

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Journal of Organic & Inorganic Chemistry
ISSN 2472-1123

2017
Vol. 3 No. 1: 2

DOI: 10.21767/2472-1123.100022

Plasmonic Study of Nanoparticles in Organic Photovoltic Cells: A Review

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Citation: Sakshum K, Kushagra K, Gauravi X, et al. Plasmonic Study of Nanoparticles in Organic Photovoltic Cells: A Review. J Org Inorg Chem. 2017, 3:1.

Abstract

The worldwide consumption of energy has increased every year by several percentages in the last decades. Nowadays, a large amount of energy is produced by fossil fuels and to a certain extent by nuclear energy. However, these resources are limited and their use has a serious environmental impact. Solar light is the most important source of regenerative energy and represents an inexhaustible energy source. Owing to this fact the attention has been drawn during the last few years towards Solar cells. Moreover, to overcome barriers such as effective cost efficiency and commercial feasibility, methods of energy generations have turned to Organic Photovoltaics devices. The advantages being: generation of cost effective devices, use of renewable sources of energy and easy flexibility. In recent years rapid development in design has led to progressive PCE of organic solar cell from 3% to almost 9-10%. To improve the efficiency of organic solar cells it is, therefore, crucial to understand what limits the cell's performance and efficiency. The scattering from the metal nanoparticles is a way of increasing the light absorption and the efficiency in organic solar cells. This review discusses the recent significant technological developments that were presented in the literature with the basic mechanisms at work, which will help improve the organic photovoltaic performance and provide an outlook to future prospects in this area.

Keywords: Organic photovoltaics cells; Surface plasmon resonance; Nanoparticles; Graphene

Received: January 27, 2017; **Accepted:** February 17, 2017; **Published:** February 20, 2017

Introduction

In the past years, the demand for clean energy resources has increased, leading to a rapid growth in the field of research and development of solar energy. Solar cells are the devices which convert the light into electrical energy [1]. Solar cells can be fabricated using organic, inorganic or hybrid materials and are divided into three different generations [2]. The First generation consists of crystalline semiconductor wafers, with a thicknesses of 200-300 µm, occupying around 90% of the solar cell market. The Second-generation solar cells are based on thin film technology having thickness, usually in the range of 1-2 µm. The Third generation solar cells are under research process, to increase the efficiency with the help of second generation solar cells. It focuses on developing ways to improve absorption and efficiency by increasing the trapping of light at desired frequency. A new method has evolved in recent times for increasing the light absorption i.e., the use of nanoparticles **(Figures 1 and 2)** for scattering light when excited at their Surface Plasmon Resonance [3-9]. Silver and Gold are commonly used plasmonic materials, and they have also been combined with oxide cores or shells.

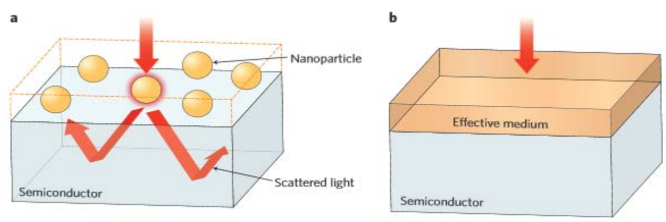

Figure 1 Plasmonic metal nanoparticles as scatterers. **(a)** Incoming light excites confined plasmons in the particles and is then scattered into the guided modes of the substrate. **(b)** An effective-medium theory model that captures the key features of the optical processes.

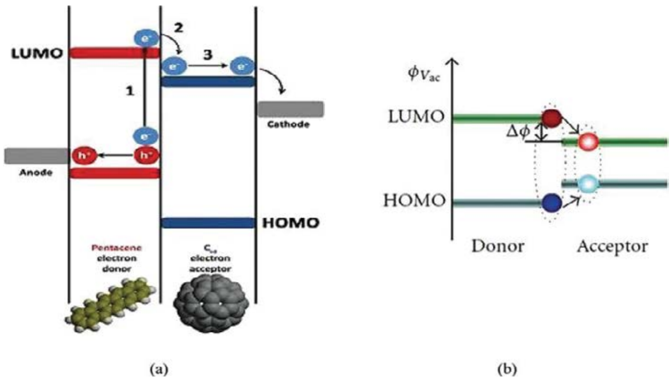

Figure 2 **(a)** Electron movement in Organic Solar cell **(b)** Band Gap of Organic Solar Cell.

Tandem organic solar cells with embedded plasmonic shows promising approach to increase the efficiency of the cells. Polymeric nano-composites incorporating graphitic nano-structures were extensively investigated for the next generation of efficient and low-cost solar cells, since such nano-materials show excellent electrical and mechanical properties, desirable carrier transport capabilities, and provides an efficient pathway to the dissociated charge carriers.

Structure of photo voltaic cell

solar cell is a device which directly converts the light energy into electricity by photovoltaic effect. Solar cells are made up of semiconducting materials which have certain characteristics in order to absorb sunlight and their electrical characteristic vary with the exposure to light. They can be made of one single layer of light-absorbing material or multi-junctions to achieve more absorption. The operation of a photovoltaic (PV) cell requires basic attributes such as: absorption of light, generation of electron-hole pairs or excitons, separate extraction of carriers, etc. An organic solar device comprises of four layers on a transparent substrate which can be either glass, polyester, plastic or many other transparent materials. It is coated with different transparent conductive oxide such as indium tin oxide, and other materials. The transparent layer is used as: transparent window layer and to collect the photo-generated holes (anode). Recently Carbon structure nanotubes (CNTs) are used as the transparent conductive layer.

The electronic structure of organic solar cells is based on π-electrons and is made from an alteration between single and double c-c bonds. The band gap of these materials ranges from 1 to 4 eV. The π-electrons has much more mobility than the σ-electrons. Due to the overlapping between carbon atoms, π-electrons can jump from band to band. The π-bands which are empty are called the LUMO- Lowest Unoccupied Molecular Orbital and when filled with electrons are called the HOMO- Highest Occupied Molecular Orbital.

Principles

The basic mechanisms for photocurrent enhancement by metal nanoparticles in organic photovoltaics are Light scattering and Near-field concentration. When photon interacts with the semi-conductor, one of the three things can happen:

(i) The photon (lower than Si band gap energy) can pass through the material;

(ii) The photon can reflect off the surface and

(iii) The photon (higher than Si band gap energy) can be absorbed by the silicon.

When a photon gets absorbed, its energy is shifted to an electron, which is present in valence band. Covalent bond exists between electron and neighbouring atoms, and thus they are not able to move far. The energy given to it by the photon "excites" it from valence band into the conduction band, where the electron is free to move within the semiconductor and hence, deficiency of one electron, termed as "hole" is created. The presence of a missing bond allows the electrons of adjacent atoms to move into the hole leaving behind another hole, which leads to generation of holes. Thus, the photon absorbed in the semiconductor develops mobile electron-hole pairs.

Once the electrons and holes are separated, they tend to recombine, as they are of opposite charge. The efficiency can be high if the electrons can be collected before recombination. The higher energy photons are absorbed by the photovoltaic cells, but due to the difference in energies, they are converted to heat [10]. One of the methods to collect the electrons quickly is to make the conducting material very thin. But if the surface of conductive material is made very thin, the device will absorb much less light. Thus, an optimum size of surface needs to be developed for absorbing the maximum photons and generating more electron-hole pairs **(Figure 3a).** Spectral ranges from 600 – 1,100 nm of the solar spectrum, is poorly absorbed. This is the reason that, wafer-based crystalline Si Solar Cells have a much larger thickness of around 180-300 µm with low efficiency. For high-efficiency solar cells, the carrier diffusion lengths must be several times smaller to the material thickness for collection of all photo-carriers.

The Photovoltaic absorbers thickness is optimized for complete light absorption and photo-carrier current collection. The standard AM1.5 solar spectrum with the graph shows that the fraction of the solar spectrum is absorbed on a single pass, through a 2-µm-thick crystalline Si film see **Figure 3b**. These requirements can be obtained in thin solar cells. Design and materials-synthesis of solar cells are opposed by these requirements i.e., optical absorption thickness and carrier collection length.

Plasmonic for Photo Voltaic's (PSC)

Plasmon's are free-electron in a conductor which oscillate, that allow light to be manipulated at the nanoscale. Plasmons have the ability to guide and confine light, enabling them to be a new design for solar cells [11-15]. Basically, the absorber layer enhances the efficiency of the organic photovoltaic cells. Plasmonic structures provide three ways of reducing the physical thickness of the absorber layers while keeping its optical thickness constant.

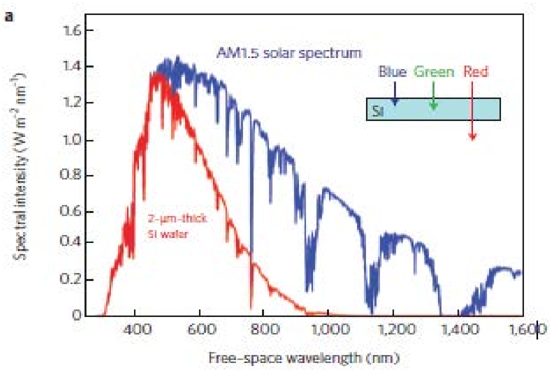

Figure 3a AM1.5 solar spectrum, with the graph that indicates the energy absorbed in a 2-μm-thick Si film. Clearly 600-1, 100 nm spectral range is not absorbed in thin Si solar cell.

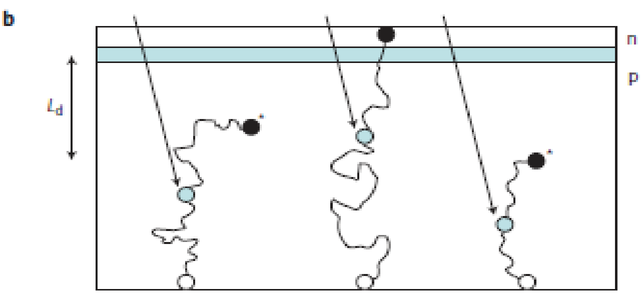

Figure 3b Schematic shows carrier diffusion from generation of photo-carriers to p-n junction. Charge carriers are far away from p-n junction and not effectively collected, thus occurring recombination.

First, metallic nanoparticles can be used as sub-wavelength scattering elements to couple and trap free waves from Sun **(Figure 4a).** Second, metallic nanoparticles can be used as antennas, in which, the semiconductor is coupled to the Plasmonic near-field, thus increasing its effective absorption **(Figure 4b).** Third, a ridged metallic film on the back surface of an absorber layer can couple sunlight into SPP mode **(Figure 4c).**

Light-trapping geometries of nanoparticle in solar cells. **(a)** At the surface of the photovoltaic cell light trapping is observed by scattering from metal nanoparticles. Light is scattered and trapped into the semiconductor thin film by high-angle and multiple scattering, causing an increase in the optical path length in cell. **(b)** Metal nanoparticles embedded in the semiconductor for light trapping by the excitation of localized surface plasmons (LSPR). The excited particles in near-field causes the generation of electron hole pairs. **(c)** Light trapping by the excitation of surface Plasmon polaritons at the surface of semiconductor. The metal back surface couples light to surface Plasmon polariton or photonic modes that propagate in the plane of the semiconductor layer **(Figure 4).**

Plasmonic: Scattering and absorption by metal nanoparticle

The principle for the functioning of plasmonic solar cells include: scattering and absorption of light due to the deposition of metal Nanoparticles **(Figure 5a)**. A thin silicon sheet does not absorb light effectively, for an increase in the absorption of thin Silicon sheet more light is required to be scattered across the surface in order to convert it into the useful electrical energy **(Figure 5b)**. It has been found that metal nanoparticles help to scatter the incoming light at resonance wavelengths across the surface of the Si substrate [16-21]. To increase the light absorption in thin film solar cells, three routes have been adopted: a) embedding nanoparticles on the surface of the solar cells, b) putting nanoparticles inside the active layer; and c) grating the back contact from the side of the active layer. These plasmons create a strong electric field around the nanoparticle and enhance the absorption in the region contiguous to it. This technique is very useful for OPV because in OPV the diffusion length is short. Thus, the placement of nanoparticles is most beneficial when placed close to the junction. The order of densities of electrons for different metals shows the type of light, which corresponds to the resonance. The surface resonance frequency for spherical particles primarily depends on the free electron density in the particle.

The resonant frequency can be shifted if the dielectric constant for the embedding medium is changed. For longer wavelength and broadened resonance range, higher indexes of refraction are needed [22,23]. Gold is highly stable and shows broader resonance peak than silver. Though silver is cheaper in comparison to gold shown in **Figure 6.** but highly unstable and gets oxidized which affects its resonance frequency. On the other hand, copper is cheaper than silver, but it is not as effective as compare to gold and silver **(Table 1).**

Plasmonic in organic photovoltaics

Plasmonic particles have been implanted between the active layers and selective contacts in OPV devices [24,25]. Typical OPVs

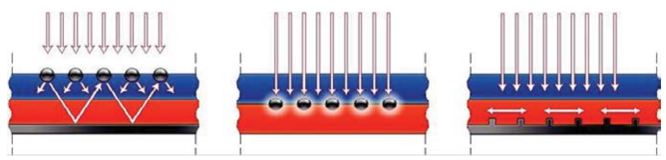

Figure 4 Light-trapping geometries of nanoparticle in solar cells.

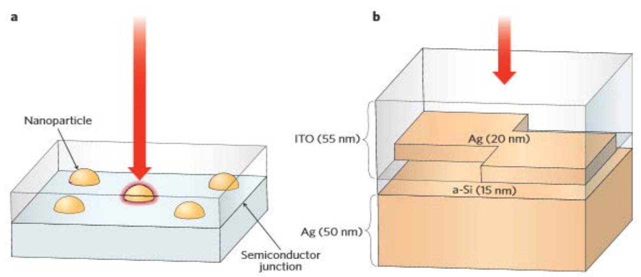

Figure 5 **(a)** Metal nanoparticles embedded in the semiconductor layer (absorber) at a cell junction to enhance the light absorption around periphery. **(b)** Unit cell of a plasmonic cell consisting of from top to bottom, an indium tin oxide antireflection coating.

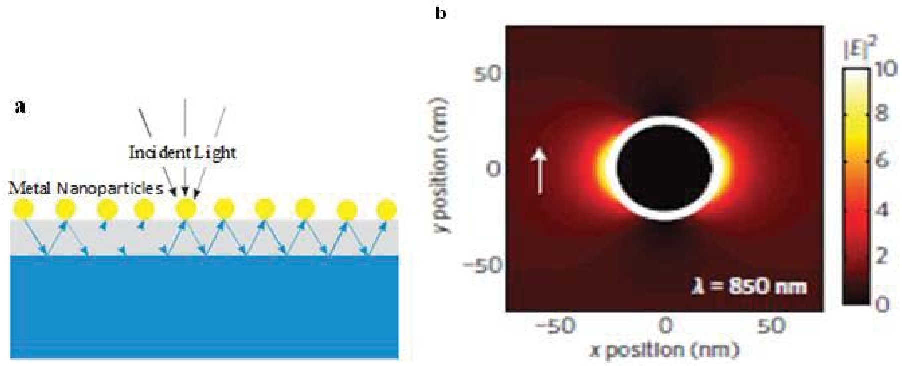

Figure 6 **a** PSC using Metal Nanoparticles. **(b)** An intense near-field of metal Nanoparticle close to the surface. Enhancement of Intensity around 25-nm-diameter of Gold particle embedded in a medium index n=1.5 with light of wavelength λ=850 nm incident (Plasmon resonance peak at 500 nm.

Table 1 Plasmonic PV's with >7 % efficiency achieved by different Metallic NP's. This work was supported by the National Basic Research Program of china (2014CB643503) and the National Natural Science Foundation of China (9133114 and 51611308).

Integrated Position	Metallic Type	Metallic Structure	Active Layer	PCE (Plasmonic)	PCE (Ref)	Enhancement	Ref.
F	Ag Au Dual	NP's NP's NP's	PTB7: PC70M PTB7: PC70M PTB7: PC70BM	8.01 8.16 8.67	7.25 7.25 7.25	10.48 12.55 19.59	[28]
F	Au	NP's	PTB7: PC70M	8.74	8.02	8.98	[29]
F	Au@Ag	Nano cubes	PCDTBT: PC70BM PTB7: PC70BM	6.31 9.19	5.29 7.95	19.28 15.60	[30]
F	Ag	NP's	PTB7: PC70BM PTB7: PC70BM	7.6 8.6	6.4 7.9	18.75 8.86	[31]
F	Au Ag	NP's	PTB7: PC70BM PTB7: PC70BM	7.02 7.52	6.23 6.23	12.68 20.71	[32]
F	Ag@SiO2	NP's	PTB7: PC70BM	8.20 8.90	7.51 7.51	9.19 18.51	[33]
R	Au	NP's	PTB7-F20: PC71BM	7.926	7.385	7.33	[34]
Dual F R	Au Ag	NP's Nano grating Electrodes	PBDTTT-CT: PC 71BM	8.79	7.59	15.81	[35]
Dual F R	Au Ag	NP's NP's	PIDT- PhanQ: PC71BM	7.5	6.65	12.78	[36]
Dual F R	Au Ag	Nano prisms	PCDTBT: PC71BM	7.06	6.06	16.5	[37]

consists of active layer i.e., Electron-donor and electron-acceptor materials. As shown in **Figures 7-9,** several donor and acceptor materials are being stated, but among these reported none of them obtains more than 3% efficiency except for PCPDTBT/PCBM and P3HT/PCBM.

Several conjugated polymers and a fullerene derivative are used in organic photovoltaic cells. Chemical abbreviations of some conjugated organic molecules i.e., PA- poly (acetylene), PPV-poly (*para*-phenylene-vinylene), P3HT- poly (3-hexyl thiophene), and a C60 derivative.

In each compound there is a sequence of alternating single and double bonds. One study shows chemically synthesized 40 nm silver nanoclusters into the activelayer of a (PCDTBT) poly[N'9'hepta'decanyl'2,7'carbazolealt'5,5'(4',7'di'2'thienyl'2',1',3benzothia-diazole):(PC70BM) [6,6]'phenyl'C70'butyric acid methyl ester Bulk Hetro junction (BHJ) solar cell to improve the efficiency [26].

The nanoclusters show absorbance peak near 420 nm. The enhanced PCE was obtained 12.7% by optimizing the w% of nanoclusters in the active layer. The enhancement was mainly due to a 7.6% increase in the short-circuit current density (JSC) and a reduction in the cell series resistance. The 70 nm truncated gold octahedral nanoparticles at optimized concentrations (5 wt.%) to the BHJ active layer [27].

Graphene plasmonics for light trapping

The efficiency of the photovoltaic cell upgrades with the increase in absorption of light in the solar cells and it can be improved

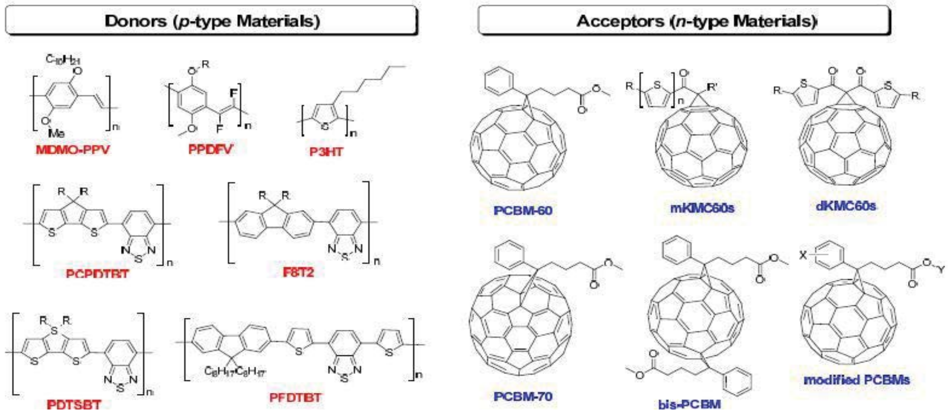

Figure 7 Chemical Structure of Organic solar cell Donor and Acceptor Materials.

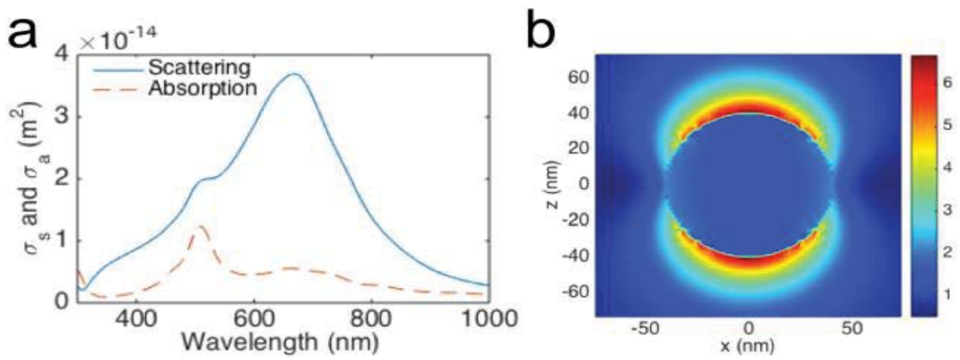

Figure 8 **(a)** Scattering and absorption cross section vs. wavelength for 40 nm diameter Ag nanospheres embedded in a PCDTBT: PC70BM background. **(b)** Calculated normalized electric field intensity (λ= 680 nm) for a single Ag nanospheres at the plane normal to the incident illumination [27].

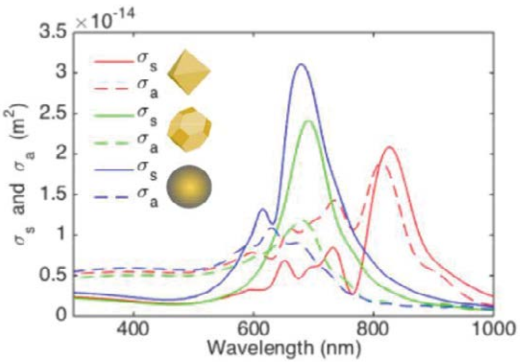

Figure 9 Scattering (solid lines) and absorption (dashed lines) vs. wavelength for different shaped plasmonic nanoparticles embedded in a PCDTBT: PC70BM. Red: 70 nm octahedral Green: 70 nm truncated octahedral Au nanoparticles. Blue: 70 nm Au nanospheres [27].

using plasmonic. The plasmonic material, recently emerged is Graphene, has shows significantly less losses compared to conventional plasmonic materials such as gold and silver. Graphene Plasmon's has the properties of collective electronic excitations, Enhances the optical absorption in its surrounding, which makes it most attractive property and highly efficient [38,39]. Even though the interaction between light and graphene is quite weak and optical absorption is about 2.3% in the visible and near infrared range, the excitation of graphene plasmons totally changes this picture [40,41]. The doped and patterned graphene support LSPR (Localized Plasmonic Resonances), leading to effective confinement of light and enhancement of local fields and provides a route to enhance light-graphene interactions.

In solar cells, the material extinction must be high to allow efficient light absorption and photo-carrier generation. On the other hand, there is a strong desire to reduce the thickness of semiconductors in order to decrease the consumption of materials and improve the performances. Plasmonic is one of the most effective routes for light trapping and absorption enhancement [42-44]. A domain of different plasmonic structures such as metallic nanoparticles [45-47], gratings [48-50], antennas [51,52] and others [53,54] have been used to improve the performance of solar cells. Graphene when compared to conventional plasmonic materials such as gold and silver has less losses and is very promising for light trapping in optoelectronic devices [55].

Recently, more than one order of absorption enhancement of doped graphene disks has been experimentally demonstrated [56,57]. Previous studies focused on engineering section of absorption in graphene and the potential of using it to enhance the absorption of other light-absorbing materials [58,59]. The excitation of localized plasmons in doped, nano-structured graphene is an effective way for light trapping and enhancing the absorption in light-absorbing materials, which may lead to a new generation of highly efficient solar cells.

Recent Advances in PSC's

One of the main targets has been on improving the thin film SCs through the use of metal nanoparticles distributed on the surface. The increased scattering provides more photon availability, which causes electron excitation and the generation of current.

Catchpole and Polman: In thin film SCs, path length enhancements up to a factor of 30 were found for optimized shapes as particle shape is a important parameter for determining the light trapping efficiency [60].

Westphalen: Improvement for silver clusters incorporated into indium tin oxide and zinc phthalocyanine solar cells [61].

Derkacs: Gold nanoparticles on thin-film silicon gaining 8.3 per cent of conversion efficiency [62].

Stenzel: Photocurrent Enhancements by a factor of 2.7 for indium tin oxide-copper phthalocyanine structures [63].

Stuart and Hall: Achieved enhancement in the photocurrent by a factor of 18 for a165 nm thick silicon on insulator photo-detector at a wavelength of 800 nm using silver nanoparticles on the surface of device [64].

Schaadt: Enhancements up to 80 percent at wavelengths around 500 nm was obtained by deposited gold nanoparticles on highly doped wafer-based solar cells [65].

Organic Solar Cells Market - An Economic Solution to Sustainable Solar Power Generation

The global organic solar cells market also commonly known as organic-based photovoltaics is a highly developing and rapidly growing market. In only a matter of a year, the market has made an impressive shift from fundamental research at university levels into industry-level production. Use of photovoltaic cells for harvesting energy directly from sunlight is considered one of the most effective ways of addressing global energy needs. Provided that solar cells can be made economically competitive against traditional energy sources such as fossil fuels, the large-scale manufacturing of solar cells will offer a reliable source of sustainable energy that could account for a substantial portion of our energy needs. Usage of organic materials such as various novel polymers for fabricating solar cells is a good way of reducing the manufacturing and thus final costs of solar cells. The use of organic substances for manufacturing solar cells makes the manufacturing process potentially easier than conventional manufacturing processes using silicon or other such materials. Organic solar cells also have one more important advantage over the conventional solar cells [66].

They can be easily molded into different shapes and colored in various ways, making them preferable when the application focuses more on design and flexibility and less on efficacy.

The only restricting factors for organic solar cells are their lower efficiency and smaller life compared to conventional solar cells. However, with technological advancements taking place at a rapid pace, the industry will also find a solution to these problems soon.

The many benefits of organic solar cells have caused the global market to rapidly adopt these cells in a variety of application areas, especially in fields such as building-integrated solar cells and mobile applications such as powering portable devices in vehicles.

Global market scenario

Analysts state that the global market for organic solar cells had an estimated net worth of US$25.518 million in 2013. Registering growth at a CAGR of nearly 21.2% between 2014 and 2020, the market is expected to reach an estimated value of US$97.412 million by 2020. On a regional basis, the European market leads the global market, accounting for a nearly 35% share of the global organic solar cells market [66]. The North American market acquires second place by accounting for a nearly 28% share in the overall market. Demand for organic solar cells is currently the highest from the building integrated organic photovoltaic (BIPV) section. This market segment is also expected to flourish at a good pace over the future years between 2014 and 2020.

Conclusions

Recent advances have shown a huge potential of Plasmonic solar cells compared to conventional silicon cells. Research in PSCs is rapidly exploiting the benefits offered by plasmonic solar cell. The advantages of plasmonic particles is to use them on any thin film SC (silicon or organic). The metal nanoparticles of different size, shape and embedding medium can enhance the efficiency of the solar cells over a large range of the electromagnetic spectrum. Also their adaptability in production methods, properties and applications looks very promising for the future of solar energy. Hence, PSCs are promising in lowering the cost of solar energy generation along with providing high efficiency.

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66 Organic Solar Cell Market by Application (2014-2020) Building Integrated Photovoltaic, Mobile Application, Conventional Solar and Defense Application - Global Industry Analysis, Size, Share, Growth, Trends and Forecast. Transparency Market research.