REVIEW ARTICLE

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A Review on the Incorporation of Nanoparticles in Polymer based Optoelectronic Devices

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Abstract

Organic solar cells (OSCs) and polymer-based optoelectronic devices have been a topic of focus for the researcher to meet the growing need for clean and economical energy. Polymer-based solar cells have been very prominent in the study of the production of organic solar cells. P3HT: PCBM has been a combination of polymers mostly used for manufacturing solar cells because of their high efficiency and accessibility. Some added assistance of metal nanoparticle coating on the solar cell has helped optimize saturation current (J_{sc}) in them. There has been a multitude of device structures tried for the optimum performance of the solar cells, with bulk heterojunction layer (BHJ) being the most fruitful in the results acquired. Incorporating metal NPS also helps stabilize the OSCs to make a more robust panel. Different studies have been carried out on the specimen used in OSCs with different advantages in the functioning of the device. This article gives an extensive overview of different OSCs and devices tried and manufactured to obtain an optimal device for commercial use.

Keywords: Organic Solar cells, Silver Nanoparticles, Optoelectronic devices.

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Introduction

Organic solar cells are very important for realizing the potential of renewable solar energy in a commercially viable manner. The amount of literature that has been in the field of research is extensive.[1] Solar cells can generate a limited amount of electricity per unit but there are still large sections of land where these solar plants can be established. In conventional solar cells, the biggest limitation has been the use of steeply-priced elements, which have made solar cells a tough sell in less privileged countries like India. Et al. estimated around 0.5 USD, 15 MJ, and 0.8 kg CO_2 under the incident energy of 1700 kWh/m^2/yr.[2] Other added advantages of the PV cell are short lead times to install and run, while the low maintenance PV cells are also highly modular and resultantly applicable over a wide range of power levels.[3] When the polymer blend is combined with metal nanoparticles (such as Silver, Copper, Manganese, Zinc, Gold, etc.) the properties of the composite are enhanced by multiple folds potentially enhancing capacitive and electrical properties.[4]

Thin film solar cells generally require less surface area for radiation absorption, and costly purification steps have provided a very suitable and valid alternative. Thin film cells have been justifiably compared favorably to silicon-based solar cells with a profound energy system and payback time.[5] It is necessary for functioning organic photovoltaic cells that their photo-generated excitons transfer nanoparticles also adds to the thermal stability of the material towards donor-acceptor (DA) heterojunction leading to dissociation into a

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free electron and hole. Thin films with metal nanoparticle coating have shown amazing characteristics for photocurrent absorption. Organic photovoltaic solar cells (OPVs) have been extremely profitable and robust in comparison to inorganic solar cells since they provide greater mechanical flexibility. They can also be molded into various shapes attributing to the flexible nature of these OPVs. Various thin films could be manufactured for their capacity to be involved in optical and optoelectronic devices. There have been multiple combinations of polymer blends that have been incorporated for the same purpose. One of those combinations is PVDF-PMMA which is dissolved well in acetone along with the Iodine and of the Lithium halides (LiI, LiBr, LiCl, etc.) along with the nanoparticles of Al_2O_3.[6] Similar films like PMMA-PVA were designed with the help of Acetone as a solvent with SiO_2 nanoparticles doped with them to enhance optical and optoelectronic properties.[9] It's been intimated that these polymeric thin films have characteristics like refractive index which gets altered with the addition of the dopant. The addition of Poly-(3-hexylthiophene) (P3HT): [6, 6]-phenyl C60 butyric acid methyl ester (PCBM) acts as an active layer in the cell which can be achieved by self-organization of BHJ materials with chloroform and toluene being used as its solvent.[7] Chlorobenzene is most widely used in BHJ structures because of its solubility of PCBM in it and its crystallization structure. [8] There have been studies on the effect P3HT: PCBM has at varying concentrations in solvents like Chlorobenzene. The variation in concentration of polymer combinations alters the crystal structure, further improving the Photovoltaics' performance. The preparation of these composites plays a very important part in modifying their functionalities by controlling the components such as concentration, structure, size, and shape of materials.

This review will focus on the addition of metal nanoparticles to various polymers that showcase optical and electrical properties leading to their use in renewable energy technology. Organic element-based devices such as light emitting devices (LED) and photovoltaic Cells have been part of great interest in the state-of-the-art research programs to replace their inorganic counterparts for multiple applications. Even though inorganic optoelectronic devices have been a very well-advanced technology that has resulted in these inorganic devices being of high-quality performance and sound stability, they require a high cost of production, especially for large-scale applications. To fix these shortcomings, organic devices come into the picture where the desirable qualities of organic materials such as low cost, availability, flexibility, etc. Specimen preparation of the optoelectronic device is given in Figure 1. A major demerit of using organic materials is that they are highly reactive and hence volatile (low stability) even at comparatively friendly temperatures. Still, a major factor in evaluating the performance of a solar cell is its lifetime and that is the reason organic materials-based devices have not been able to make it to the general market. Various processes for degradation of organic devices have been identified: diffusion of electrodes, photo and chemical oxidation, and thermal volatility. Measures taken to improve these drawbacks include incorporating metallic nanoparticles onto the precursor polymer. This incorporation increases the specimen's stability and enhances optical properties and electrical conductivity due to the addition of nanofillers at varying concentrations and shapes for different applications of devices, and the creation of a pathway for charge carriers.[10]

Photoactivation

Photocatalysts are also a very important consideration under the requirement of a functioning solar cell. But there is a problem, Transition metal oxides (TMOs) activate only at ultraviolet radiation and this radiation only comprises 5% of the total surface energy at the earth's surface. There have been serious attempts to enhance the region of activation

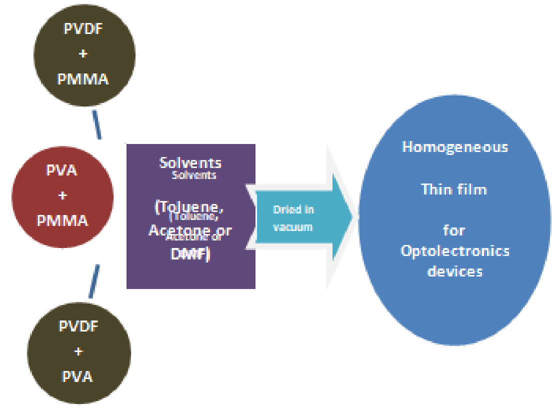

Figure 1: Flow chart of the preparation of Optoelectronic device with the help of different polymers

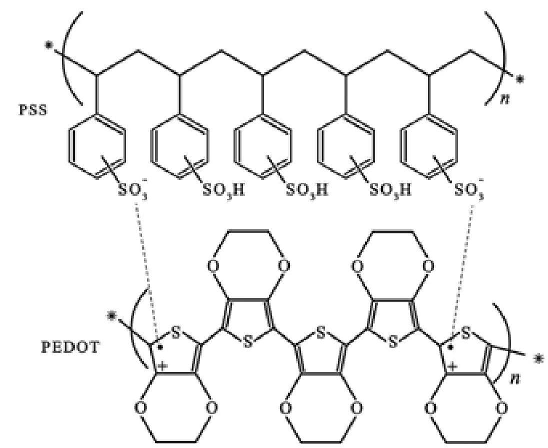

Figure 2: Chemical structure of PEDOT: PSS.[28]

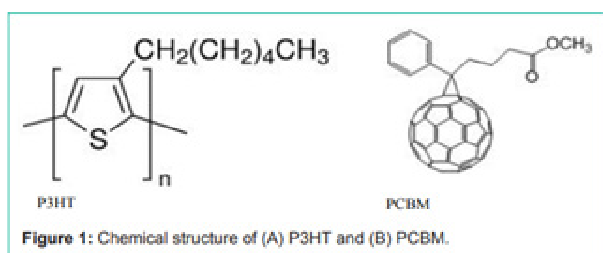

Figure 3: Chemical Structure of a) P3HT b) PCBM[28]

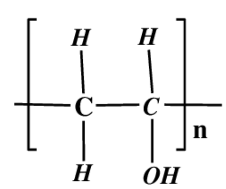

Figure 4: PVA structure[35]

of these TMOs. To achieve this, photosensitizers are used by adding (doping) the material, photosensitize the surface, or introduce molecular absorbers. Photosensitizers have a smaller band gap and higher conduction band in comparison with wide-gap TMOs.[12] Photoactivity can be extended to

Table 1: Summary of the nanocomposites prepared with various polymers and nanoparticles.

Author	*Polymer*	*Nanoparticles*	*Size (nm)*	*Reference*
Suman sarkar	PEDOT: PSS	AgNP	7	21
Suman sarkar	PEDOT: PSS	AuNP	22	21
Sang hoon oh	PEDOT: PSS/P3HT: PCBM	ZnO NP	35	43
Ravindranadh koutavarapua	PVA	ZnO NP	12	26
Gharibshahi L.	PVA	AgNP	8	33
Y. Z. N. Htwe	PVA	AgNP	15–55	27
Agnieszka Iwan	PEDOT: PSS	AgNP	60	46
Syed khasim	PEDOT: PSS	AuNP	20	62
Ramesh	PEDOT: PSS	TiO2 NP	50–200	61
Long quoc pham	PEDOT: PSS	Cu NP	56	22
Pulit-prociak	PVA	Cu NP	300	47
Alaaldin M	PVA	AuNP	23–79	48
XU ning-ning	PVP	AuNP	55nm	49
Mirzaei, A	PVP	AgNP	40–80	50
Maoping zheng	PVP	AgNP	55nm	51
Poonam makwandi	PMMA	AgNP	6.6nm	52
Kenichi hayashida	PMMA	ZnO	15nm	53
Shabnam dan	PMMA	$MnFe_2O_4$ NPs	11nm	44
Nour alnairat	PVDF	AgNP	71nm	45
Soheil mansouri	PVDF	ZnO	<100	54

the visible spectrum by photosensitization. To achieve the best design a device of large intrinsic conductivities and absorption is needed to be made by combining a donor and an acceptor into a donor-acceptor (DA) heterojunction layer.[13,14] The electrical and optical properties of this donor-acceptor (DA) combination is dependent upon the wavefunction of the isolated (HOMOs) and (LUMOs) and their relative alignment. Several chemicals could be incorporated to achieve such conditions, some of the work that's been done in this field has focused on Polythiophene(Pth).[11]

Classification of Polymers for Optoelectronic Applications

PEDOT: PSS or Poly (3,4-ethylenedioxythiophene): poly (4-styrene sulfonate) is a conducting polymer that is soluble in water and most major organic solvents. It is a material that is highly flexible, processable in solution, highly transparent in the visible region, and has good printability.[15] It has a granular structure in which PSS of high molecular weight are linked electrostatically with PEDOT segments. Those PEDOT: PSS grains are encompassed by excess PSS neutral specimens. These neutral species fill the area between the PEDOT: PSS grains.[16] It plays an important part as interfacial layers that are used to extract holes in organic devices as well as mixed with polar organic solvents to perform the role of a transparent electrode in organic optoelectronic devices. In the literature, we find that PEDOT: PSS exhibits high conductivity that scales up to 1418 S cm^{-1}.[17] There have been studies to learn about the development of electronic properties and morphology of PEDOT: PSS due to variations in the controlling process. Along with that, improvement in conductivity to the level of ITO for achieving plastic and ITO-free optoelectronic devices.[18,19] Another important parameter that needs to be optimized for this polymer to have a good optoelectronic performance is an optimal work function that needs to be synchronized with an anode to increase the injection and extraction.[20] present an interesting method to enhance these properties by adding AgNPs because of the interaction between PSS and AgNPs. Methods used to make PEDOT: PSS-AgNPs nanocomposite includes inject printing method where the contact between AgNPs and PEDOT is maximum. Other metal nanoparticles that have been treated with PEDOT: PSS is Gold nanoparticles[21] CuNPs[22] and SnO NPs.[23]

P3HT: PCBM is the most important and widely used polymer in solar cells for its superior conductivity and stability. poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61butyric acid methyl ester (PCBM) have shown the highest efficiency up to 4–5%, Such good efficiency performances can be achieved with the help of processes like annealing and thermal treatment.[24] Optimization of thermal conditions determines the organization of polymers and morphology and greatly impacts the electrical and optical performance of electric and optical devices. But these prolonged thermal processes elongate the devices' fabrication time, making them less accessible.[29] Chemical Structures of PEDOT: PSS, P3HT:PCBM, and PVA are given in Figures 2, 3, and 4, respectively.

PVA is a very important and readily used polymer for polymer nanocomposite. It shows high transmittance, easier processability, and nontoxic preparation due to its solubility in water. It performs the role of chemical stabilizers in metal composites because they prevent agglomeration and precipitation of particles. Adding nanoparticles to it helps in film casting as reported by Khanna *et al.*[25] where they used mild reducing agents like sodium formaldehydesulfoxylate (SFS) to reduce $AgNO_3$ and embed it with PVA. They found SFS to be very effective as a reducing agent for the preparation of PVA–AgNPs composite due to SFSs weaker reducing nature as compared to other reducing agents like hydrazine hydrate. Multiple nanoparticles have been tried with PVA: AgNPs, Mn NPs, ZnO NPs, etc. Koutavarapua *et al.*[26] discussed the preparation of Al_2O_3 treated PVA doped ZnO NPs by co-precipitation method. Those nanosized composites have proven to be useful in optoelectronic devices. According to their work, a great amount of oxygen vacancy is generated due to the addition of Al_2O_3 in ZnO. The prepared samples were observed to be quite harsh at a surface that can be attributed to the capping of PVA. PVA ZnO nanoparticles possessed semiconducting behaviour. Y.Z.N.Htwe et al. [27] made silver-based PVA capped nanoparticles and reported the structural properties of their samples. They concluded that the electrical conductivity of nanocomposites was comprehensively more than those of pure polymer. Some works observed the cyclic voltammetry response where the potentiodynamic curves of stainless steel dipped in 0.1 mol L^{-1} HCl solution without and with inhibitors processed in the potential range of ±200.0 mV versus E_{corr} [30] with the hysteresis loop of Ag/PVA (in HCl) being much more narrow as compared to HCl alone. They found the PVA and PVA/AgNPs coatings to be similar, the property that they attributed to macromolecular chains at high potential values.

PVP is a polymer of monomer *N*-vinylpyrrolidone that is soluble in water. Due to its significant polarity, it has great binding to other polar molecules. When added with nanoparticles, PVP not only acts as a reducing agent for $AgNO_3$ but also behaves as a capping agent of the Ag nanoparticles.[33] Capping agents prevent the agglomeration and oxidation of nanoparticles. There is another undesirable activity of the nanoparticles that can be mitigated by capping agents: capping agents help in controlling the release of ions from the surface of nanoparticles. It also impacts the physiochemical properties of the nanoparticles and impedes their interactions with the surrounding solvent or substrate on which the nanoparticles are formed.[31] Capping agents can stabilize nanoparticles through hydration forces, depletion, electrostatic, steric, and van der Waals forces. [32] Since PVP is a chargeless polymer it has a great liking for metal atoms like Ag and Au, resulting in a great release of metal ions, making PVP a great reducing agent for such metals. Ana I. Ribeiro *et al.*[34] prepared PVP/AgNPs dispersion in ethanol and water using the exhaustion and spray method on DBD plasma-treated polyamide 6,6 (PA66) fabrics. These PVP/AgNPs nanocomposites have proven to be very efficient in antimicrobial studies when treated with a gram-positive bacterium.

PVDF is a non-reactive fluoropolymer produced by the polymerization of vinylidene difluoride that has fantastic piezoelectric properties. It has a low dissipation factor and high permittivity and enhances the magnetic activity of electromagnetic waves. [36] It also displays a high permeability, good surface porosity, and pore structure. ZnO nanoparticles treated with PVDF exhibit a wide band gap and large exciton radius, rendering them very useful in dye-sensitized solar cells, piezoelectric materials, sensors, etc. These composites prove to be very interesting in the field of pyro and piezoelectricity since both PVDF and ZnO exhibit good pyroelectric behavior. Many efforts have also been to prepare nanoparticles – PVDF composites using the phase inversion method. In this method, a small number of nanoparticles are used to improve the performance of PVDF membranes. Different nanoparticles that have been incorporated in the PVDF include Fe_3O_4 [37], SiO_2[38], TiO_2[39], and AgNP with these PVDF membranes have also been used to inhibit the bacterial growth.[40]

PMMA is a transparent and amorphous polymer from the acrylate family with great optical properties and compatibility with biotic components.[41,42] PMMA is preferred as inks and coatings because it has moderate properties and easy processing. AgNPs treated PMMA are very valuable because of their optical properties. Since Silver and Gold nanoparticles show size-dependent optical properties which has been reported by a multitude of authors as given in Table 1. Silver is a great conductor of electricity and provides many physical, mechanical, and optical advantages as well. As we have discussed earlier, there is a challenge of aggregation in polymers which can be solved by introducing Ag or Au nanoparticles. This aspect of polymer synthesis can also be overcome by a surface modification which modifies and improves the interfacial interaction between nanoparticles and polymer.

Effect of Nanoparticles in Polymer Nanocomposites

Nanoparticles especially metal ones are readily used to enhance the efficiency of optoelectronic devices. The absorption band of surface plasmon resonance for AgNPs lies between 400 to 450 nm and for AuNPs lies between 500–600 nm which also depends on the size, shape, and inter-distance of nanostructures.[55] AgNPs come in different shapes like decahedrons, icosahedrons, spherical, etc. Decahedral AgNPs: PEDOT: PSS composite shows more roughness and higher efficiency because of its higher propensity to collect holes and leading to a stronger surface plasmon resonance. It results in a hike in the efficiency of about 12% in comparison to the lone PEDOT: PSS layer.[56] This increase in efficiency can be attributed to the mitigation of electron-hole pair generation which moves to the cathode and anode and affects the efficiency. However, Spherical AgNPs have shown a clear increase of about 16% in efficiency where there is no observable agglomeration of nanoparticles that is not the result of the concentration or SPR (Surface Plasmon Resonance) effect of AgNPs but due to the increased conductivity in the specimen.[57] Moreover,[58,59] worked on optimizing the size of AgNPs for optimal efficiency, and it was observed that AgNPs of 30nm show better efficiency at the concentration of 0.025 wt% in PEDOT: PSS whereas 60 nm AgNPs showed similar performance without much improvement on the smaller NPs. These characteristics could be attributed to the larger size of nanoparticles which augments the hole injection but in the case of 60 nm, AgNPs the larger size alters the Localised Surface plasmon resonance resulting in stunting the growth in the hole injection process. The surface plasmon effect of metal NPs enhances photo absorption length, scattering, and trapping of incident light. The mixture of Silver and Gold nanoparticles has shown even better performances compared to any device made of only one kind of nanoparticles since by incorporating both metals, we can harness the absorption region of both.[60]

Conclusion

Organic and polymer-based optoelectronic devices are significantly more eco and budget-friendly but face challenges in terms of stability because the organic matter is more reactive to the environment. Other challenges faced by organic devices include efficiency, light absorption, and light coupling. One of the most promising solutions to these challenges is incorporating Metal nanoparticles with the polymer films or specimens. These nanoparticles can increase the photon absorption and light coupling without increasing the thickness of the layer. The mechanism behind these augmentations can be attributed to the enhanced light scattering process or surface plasmon resonance. The impact of SPR on the electronic properties of optoelectronic devices remains a work in progress.

This review showcases the recent work done in the field of metal nanoparticle incorporation in various polymers for applications in devices like OLEDs and OPVs. Nanoparticles enhance the optical properties by increased scattering, plasmon polaritons, etc. Nanoparticles also increase electrical properties like hole injection and conduction through charge dissociation. Moreover, morphological properties also play a tremendous role in the quality of such optoelectronic devices. Further study and development will help in opening new avenues in this technology of harvesting renewable energy.

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