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Improvement in the Photosensitivity of MEH-PPV by Incorporating ZnO Nanoparticles of Different Morphology for Photovoltaic Application

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ABSTRACT
In this study we have synthesized ZnO nanoparticles of rod-like, sphere-like and flower-like structure in solvothermal route by using different capping agent. With the help of XRD data, using Shearer's equation the average particle size of different morphologies were calculated as 86, 57 and 26 nm for flower-like, sphere-like and rod-like ZnO respectively. The direct band gap energies of the nanoparticle were calculated as 3.46 eV, 3.65 eV and 3.68 eV by using Tauc's plot. Electrical property of MEH-PPV thin film with ZnO NP (flower, sphere and rod like structure) was studied by measuring the dark and photo conductivity of the material and their applicability as an active layer of organic-inorganic hybrid solar cell was also studied. The photoconducting behaviors of MEH-PPV and as synthesized ZnO nanoparticles of different morphology were compared for the application of organic-inorganic hybrid solar cell. This study reveals that the composite film prepared with MEH-PPV and wide band gap ZnO sphere like structure show highest photosensitivity.

Keywords: Solvothermal synthesis, ZnO nanoparticle, morphology, photosensitivity, hybrid solar cell.

1. INTRODUCTION

In the last few years there has been a tremendous effort to develop inorganic semiconducting nanoparticles with their application in organic-inorganic hybrid solar cells to reduce the cost by optimizing the active material. Several inorganic nanoparticles were successfully applied to develop solar cell [1,2]. Among the inorganic nanoparticles, ZnO is a nontoxic n-type wide bandgap semiconducting material [3] which was applied efficiently in thin film transistors [4], light emitting diodes [5], optical sensors [6,7] as well as in photovoltaics [8]. Since the band gap energy of ZnO nanoparticle is wide and exciton binding energy is too high (60meV) [9] with high optical transparency [10], it was selected as one of the promising material in fabrication of organic inorganic hybrid solar cells [11]. The large excitonic binding energy of ZnO leads to extreme stability of excitons at high temperature [12] and enables the devices to function at low threshold voltage. Another important property of ZnO nanoparticle is the tunability of electron mobility [13] by optimizing the particle shape and size. Nanomaterial with a suitable band gap for a particular device application can be prepared by changing their morphology. The absorption depends on the effective surface area of the absorbing materials, which results the change in direct band gap. According to Burstein–Moss effect, depending upon the morphological growth of nanoparticles [14] the absorption edge is pushed to higher energies, as a result of all states close to the conduction band being populated. The higher band gap material is more superior in transition of excitons at above the room temperature.

ZnO nanoparticles of different morphology have been synthesized by different groups. Flowershaped, prism like, rod like, snow-flakes like ZnO nanoparticles had been reported by Zhang et al.[15] Gao et al. reported flower like ZnO by thermolysis technique.[16] Yang et al. presented the synthesis of flower shaped, disk and dumbbell-like ZnO structures by the assistance of capping molecules.[17] In this paper we described the synthesis of flower like, rod like and sphere like ZnO nanoparticles by using solvothermal technique with varying only the capping agent.

The main objective of this paper is to study the effect on electrical and optical properties of the conducting unsaturated MEH-PPV [poly (2-methoxy-5(2- ethylhexyloxy)- phenylenevinylene] incorporation with ZnO (NP) of different morphology, which has attracted a great interest in its applications in solar cells [18]. MEH-PPV polymer has a high hole mobility but low electron mobility [19] with HOMO energy at -5.1eV and LUMO energy at -2.7eV. The intrinsic carrier mobility imbalanced in MEH-PPV severely limits the performance of polymer based solar cells. To overcome this imbalance, ZnO can be selected as one of the best semiconducting materials with band gap 3.37 eV has been used as an electron acceptor. The charge transfer mechanism in a MEH-PPV:ZnO based solar cell has been shown schematically in Fig.1. In our present work rod, sphere and flower like ZnO nanoparticles were synthesized by solvothermal technique and were applied with MEH-PPV in fabrications of active layer of hybrid solar cell. We have studied the variations of absorption, conductivity and photosensitivity of the polymer-NP composite material

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due to the change in morphology of ZnO nanoparticles.

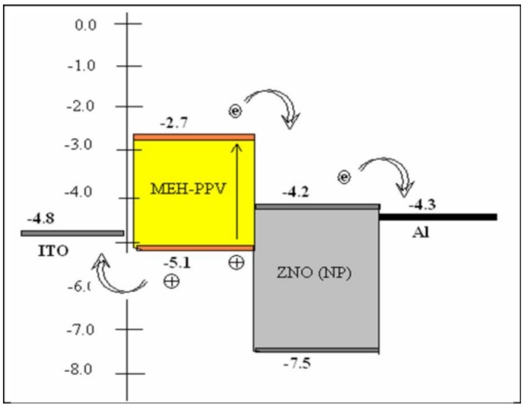

Fig.1. Schematic diagram of charge transfer procedure in MEH--PPV:ZnO solar cell

2.1. Synthesis of ZnO nanoparticles of different morphology:

ZnO nanoparticles of different morphology were synthesized by using the procedure proposed by Bahnemann et al. [20] and have also been adopted by various other groups [21,22]. In a typical synthesis of surfactant-coated ZnO nanoparticles, in 20ml methanol, 1mM(0.05g) $Zn(ac)_2$:$2H_2O$ was dissolved by vigorous stirring at about 50 ^{0}C and diluted to 200ml followed by cooling to room temperature. The solution was then divided to three aliquot volumes, each of which was taken in separate flasks. Specific surfactant **TOAB**, **CTAB**, **PVP** was added respectively into the above pre-marked solution under vigorous stirring. 0.02M, 15ml NaOH solution in methanol was added drop-wise to each of the mixture within few minutes under stirring. A white ppt was formed, which was found to be stable, at ambient conditions. Each ppt was then transferred to linear autoclave and was heated at 160 ^{0}c for 2 days. There after the solutions were washed with distilled water and ethanol repeatedly to extract ZnO nanoparticles by centrifuged technique and were dried at about 150^{0}C. In analytical measurements, powder XRD of ZnO nanoparticles were recorded. The different morphological structures were depicted by using scanning electron microscopy (SEM). The optical transmission of the nanomaterials were measured in the wavelength range of 300 –700 nm, whereas in fluorescence studies, the emission spectra were recorded. The average particle size of each sample was determined from XRD- spectra using scherrer’s broadening equation. The average size of the ZnO nanoparticles prepared by this method is between 100 nm to 10 nm. All the reactions were carried out in identical conditions at room temperature. The band gap of rod, sphere and flower like ZnO NP were calculated with the help of Tauc’s plots from UV-VIS absorption spectrum.

2.2. Fabrications and characterizations of MEH-PPV:ZnO nanocomposite thin films:

To study the optical and electrical properties of the active material the solutions of MEH-PPV and ZnO nano-particles of different morphology, were prepared separately in chloroform with a concentration of 15mg/mL and 3mg/mL respectively, ultrasonicated for 10 min at room-temperature. Once the solutions were ready, MEH-PPV and ZnO nano particle were mixed with appropriate weight ratio 2:0.1 to get the desired composite. Before preparing the thin film the mixture solution was ultrasonicated for 30 minutes. Prior to film preparation, the glass and ITO coated substrates were cleaned properly with soap solution, acetone, ethanol and distilled water accordingly and then dried in vacuum oven at 80^{o}c for 30 min. The active thin layers were prepared via spin coating of the blend solutions of MEH-PPV:ZnO (of different morphology) at 1300 rpm for 2min in open atmosphere and the devices were dried at room temperature. After that the thin film were annealed at 120^{o}c under vacuum. MEH-PPV was purchased from Sigma Aldrich and used as received. Aluminum electrode used as a cathode in thin film, was deposited on to the thin layer by thermal evaporation technique through shadow mask. To avoid the various contaminations all the samples were prepared under identical conditions. Keithley 2400 source meter was used to study the current-voltage (I–V) characteristics under dark and illuminated (100 mW/cm^2) conditions of the thin film materials. To determine band gap using Tauc's plot of the samples absorption were studied. The effective change in band gap energy, incorporation with the donor polymer (MEH-PPV) was measured aptly by observing their photo luminescence energy quenching. To study the electrical properties of the composite materials, the photosensitivity were measured by measuring current-voltage characteristics under dark and light. Vapor deposition of Aluminum electrodes were carried out by 12A4D HHV Vacuum coating unit.

3. Results and Discussions:

3.1. XRD analysis of ZnO nanoparticles:

As synthesized ZnO nanoparticles of different morphology (rod like, sphere like and flower like) were characterized by powder XRD data, recorded with the help of Bruker D8 X-Ray Diffractometer with Copper (Cu) as a target material. From the XRD data as recorded, the responsible major (hkl) planes of ZnO nanoparticles for the diffraction are (100), (002) and (101) at an angle 2θ = 32, 34.6 and 36.4 Degree. The XRD spectra of ZnO nanomaterials with different morphology (given in Fig.2.(a), (b) and (c)) as recorded were supported by the JCPDS Card No:36-1451. From these spectra it is clear that there is no significant change in diffraction pattern except the relative intensity. For the (002) plane the variation of intensity is quite noticeable. It may due to their effective surface area depending upon morphology. Using XRD data and applying scherrer's broadening equation, the average particle size of the ZnO-flower, ZnO- sphere and ZnO-rod like NPs are calculated as 86nm, 26nm and 57 nm respectively

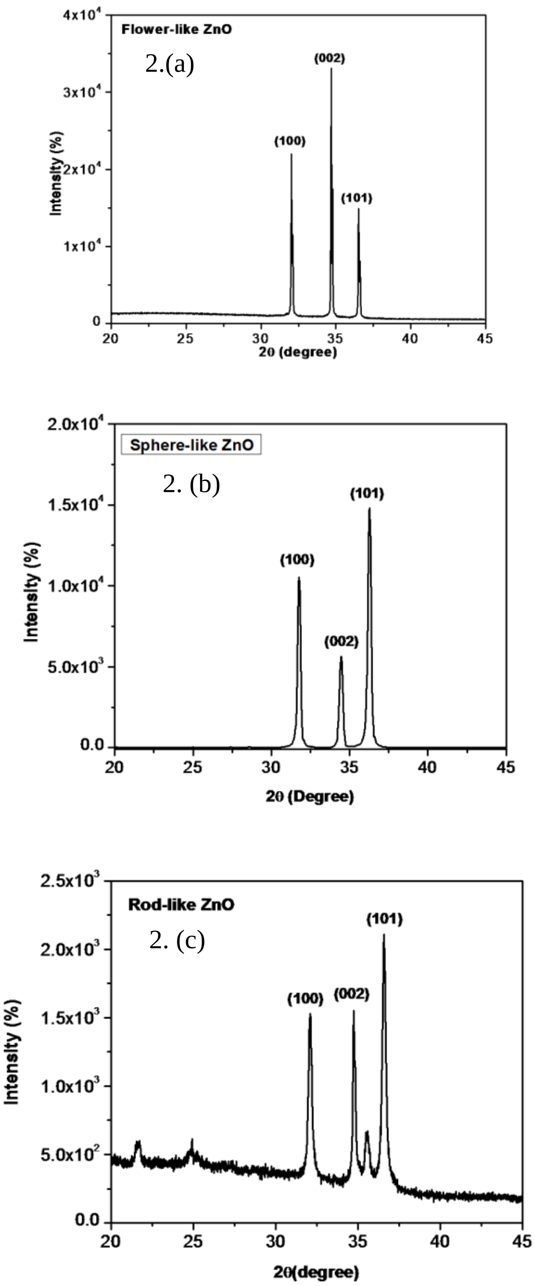

Fig. 2. Powder XRD Spectra of (a) ZnO Flower, (b) ZnO Sphere, and (c) ZnO Rod.

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3.2. Scanning Electron Microscopic images:

The analytical size from xrd were depicted by the SEM images of the synthesized nanoparticles (given in Fig.3 (a),(b) and (c)). From these images it is very much clear that the shapes of particle are flower-like, sphere like and rod-like with their dimension in nanoranges. The flower like structure was formed by the coagulations of ZnO flakes, which are not uniform. The ZnO nanorods are of average length 80-120nm with hexagonal cross-section.

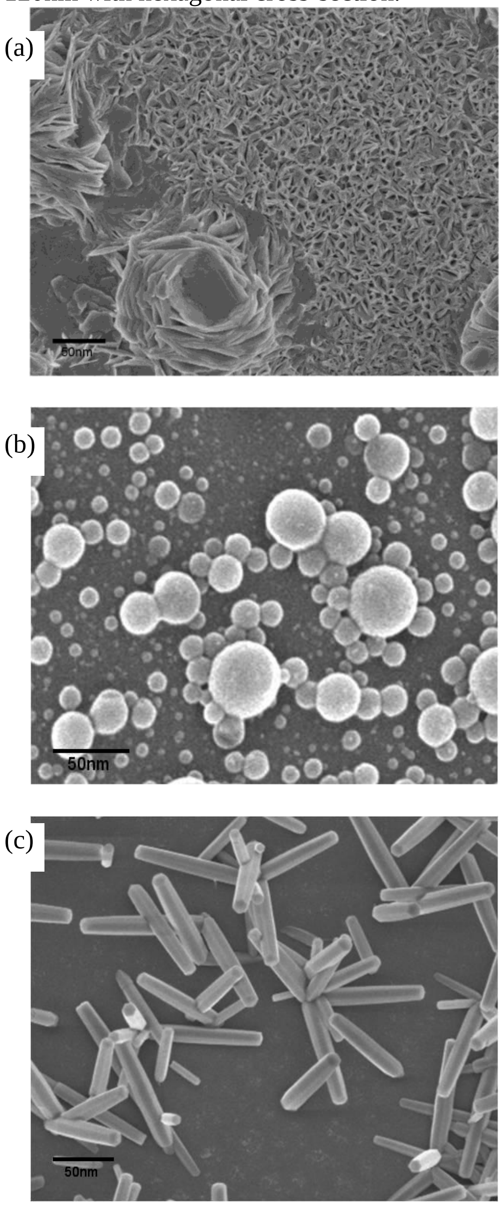


Fig. 3. SEM Images of (a) ZnO Flower, (b) ZnO Sphere, and (c) ZnO Rod.

3.3. UV-VIS Transmittance and Direct Band gap:

The transmittance spectra of the nanoparticles (of different morphology) in chloroform medium were recorded in the wavelength range of 300–600 nm with the help of a spectrophotometer 2401PC from Shimadzu (given in Fig. 4.). From these spectra it is clear that the rod like nanoparticle transmits larger part of the incident radiations in comparison to flower and sphere like ZnO NP. Considering the transmittance data, with the help of Tauc's equation direct band gap of samples were measured as 3.68eV, 3.46 eV and 3.65 eV respectively (plots are given in Fig.5(a), (b), (c).) for sphere, flower and rod like morphology.

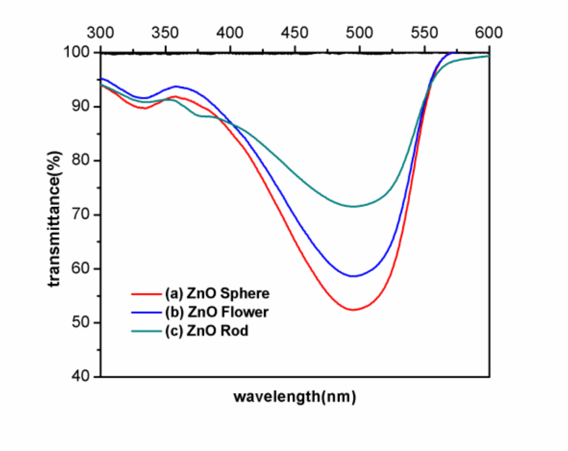
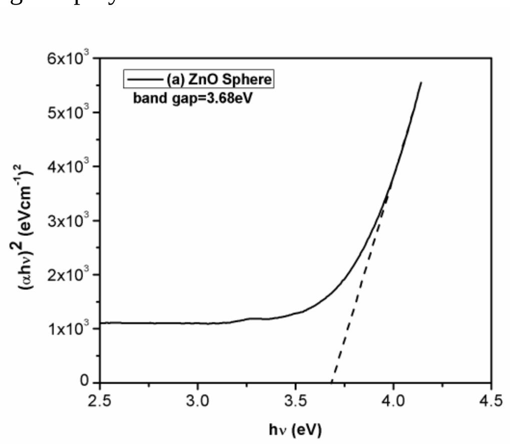
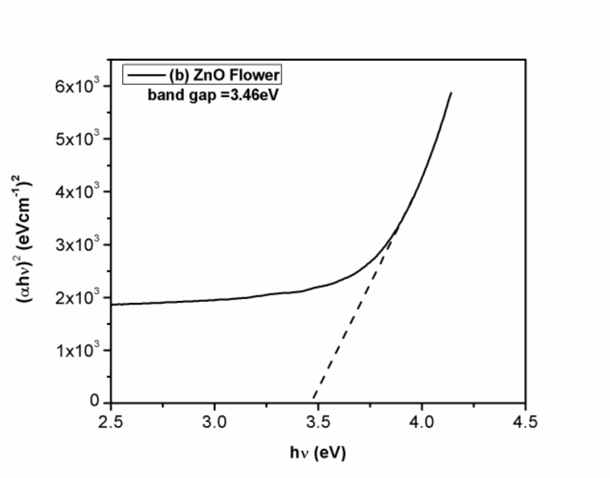


Fig. 4. UV-VIS Transmission spectra of (a) ZnO Sphere,(b) ZnO Flower, and (c) ZnO Rod.

For photovoltaic application in higher temperature, inorganic semiconductor drew a much attention due to their wide direct band gap. As the direct band gap energy was significantly changed in case of spherical and rod like structure depending upon their morphological change, which may results the high absorption edge, for the populations of all states close to the conduction band. Hence one can conclude that spherical like structure is more preferable in high temperature application of hybrid solar cells with organic polymer.





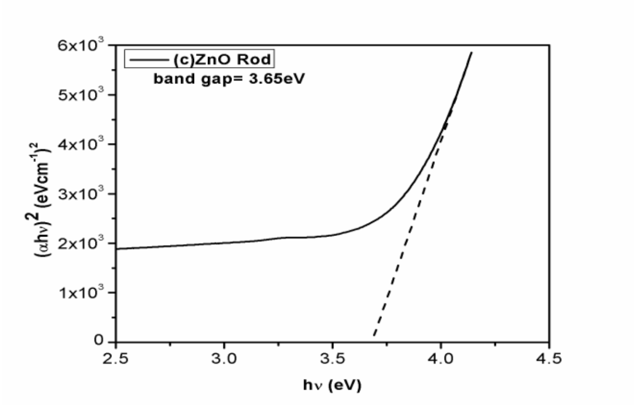


Fig.5. Direct Band gap of (a) ZnO Sphere, (b) ZnO Flower and (c) ZnO Rod by using Tauc's plot.

3.4. Characterization of MEH-PPV: ZnO nano-composite material:

3.4.1. UV-VIS absorption:

To optimize the photo sensing behavior of MEHPPV, UV-VIS absorption spectra in the range 300-700nm was recorded with the help of spectrophotometer (given in Fig.6.). From these spectra the excitation wavelength 466.7nm for MEHPPV was observed with corresponding energy 2.6 eV. Using Tauc's plot, from absorption spectra the direct band gap was measured as 2.02 eV (given in Fig.7.).

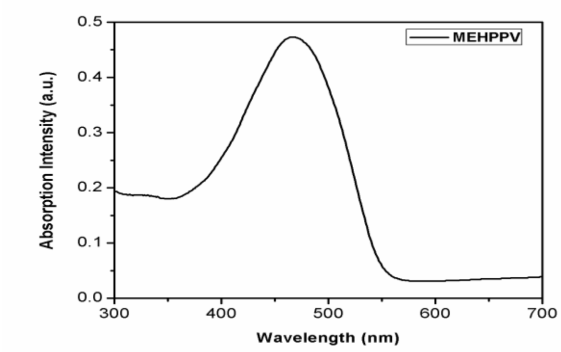


Fig. 6. UV-VIS absorption spectra of MEHPPV in chloroform medium.

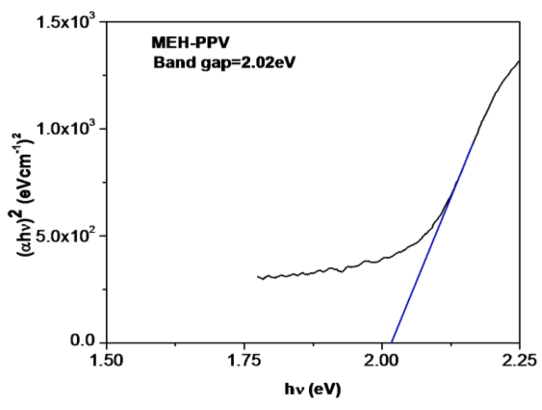


Fig. 7. $(\alpha h\gamma)^2$ vs hγ plot of MEHPPV to measure the Band Gap by using Tauc's theory.

3.4.2. Photo-Luminescence and Quenching:

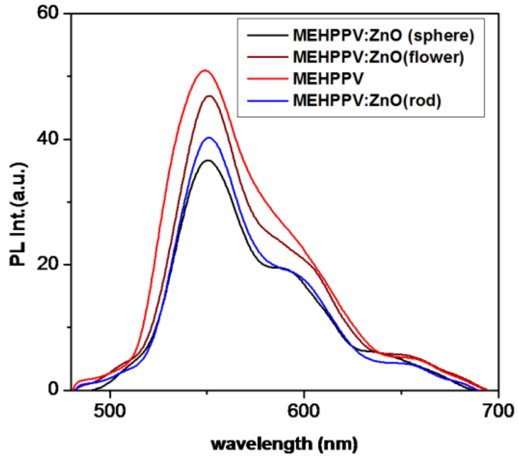


Fig.8. Photoluminesence Spectra of MEH-PPV & MEH-PPV with (a) ZnO Flower, (b) ZnO Sphere, (c)ZnO Rod in chloroform medium.

To study the change in luminosity of MEHPPV incorporation with ZnO nanoparticles of different morphology was recorded by Varian Fluorescence Spectro-photometer (Carrier Eclipse). Fig.8. represents the PL-intensity at different wavelength of MEH-PPV and MEH-PPV composites with ZnO NP in chloroform medium. The PL intensity diminished due to the energy quenching from organic donor to inorganic acceptor during formation of composite with ZnO nanoparticles at room temperature. This result confirms that the charge transfer is maximum for MEH-PPV, ZnO sphere like system.

3.4.3. Photo-sensitivity and photo conducting behavior:

To study the photo sensing properties of the organic donar polymer with and without ZnO nanoparticles of different morphology the photo conductivity and dark conductivity under white light illumination were measured with the help of Keithley 2400 source meter. As the photosensitivity (ratio of photoconductivity and dark conductivity) is an important parameter to check the applicability of a material in solar cell, we have measured this quantity for MEH-PV:ZnO NP systems and the results are summarized in Table I. Incorporation of sphere like ZnO nanoparticle with polymer (MEH-PV), the photosensitivity as well as the photo conducting property of the blended composite has been changed significantly. In the bulk heterojunction (BHJ) concept the dissociation of exciton depends on the effective junction area between organic donor and inorganic acceptor. For sphere like structure this area is maximum. The flower like morphology forms due to the combination of various number of ZnO fellings, its apparent surface area is quite larger compare to sphere and rod like morphology. But the effective junction area between polymer and ZnO NP is much greater for sphere like morphology. As the photo-current of the composite significantly changes due to interaction with incident photons, composite material MEH-PPV:ZnO(NP) with sphere like morphology is the most suitable candidate in application of hybrid solar cells.

Table1: Conductivity and Photosensitivity data

Sample	*Dark Conductivity X 10⁻³ (Scm⁻¹)*	*Photo Conductivity X 10⁻³ (Scm⁻¹)*	*Photo Sensitivity*
MEH-PPV	7.38	12.08	1.64
MEH-PPV+ZnONP (Flower Like)	14.52	127.02	8.74
MEH-PPV+ZnONP (Sphere Like)	12.52	182.80	14.6
MEH-PPV+ZnONP (Rod Like)	12.28	151.78	12.36

4. Conclusion:

In this study we have synthesized and characterized ZnO flower like, sphere like and rod like nanoparticles for the application in organic-inorganic hybrid solar cell. By using these nanoparticles of different morphology we have developed MEH-PPV:ZnO composite material for the application as an active layer of solar cell. The photo sensitivity of MEHPPV was increased by 8.9 times due to incorporation of sphere like ZnO. The study reveals that ZnO sphere like structure for its high photo-sensing behavior, is the suitable one compared to rod and flower for the application in MEH-PPV:ZnO based organic-inorganic hybrid solar cell.

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