Thesis Title:	**Design of Semiconductor/ Oxide Photoanodes for Effective Light Scattering and Charge Transfers in Dye- Sensitized Solar Cells**
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Thesis Overview

Chapter 1: Introduction

This Chapter addresses the recent advancements in design and development of photoanodes with various semiconductors/oxides of submicron/micron size of diverse morphology with favorable band alignments, which enhances the light harnessing efficiency of the photoanode by increasing the events of interaction between the sensitizer and the incident light as well as hinders the reverse tunneling of photo-injected electrons. A brief discussion on the evolution of photovoltaic technology, basic architecture and working principle of dye-sensitized solar cells are included. Role of submicron/micron size semiconductors/oxides heterostructures in light harvesting through scattering phenomenon have been discussed.

Chapter 2: Experimental

This chapter deals with the detailed synthetic protocols for materials, instrumentation techniques and methodologies used for material characterization, photoanode preparation, and device characterization using specific instrumental techniques/methods. Basic/Specific instrumentation for device characterization e.g. Newport ORIEL Sol3A solar simulator having 450 W Xe-short arc lamp equipped with AM 1.5 G filter connected to a Keithley 2400 sourcemeter for J-V curves, Newport Oriel IQE-200 having 250 W QTH lamp source for incident photon-to-current efficiency measurements and electrochemical impedance spectroscopy (EIS) measurements are also discussed.

Chapter 3: Dual function of silica nanospheres in enhancing the photovoltaic performance in ZnO nanoparticle based dye-sensitized solar cells

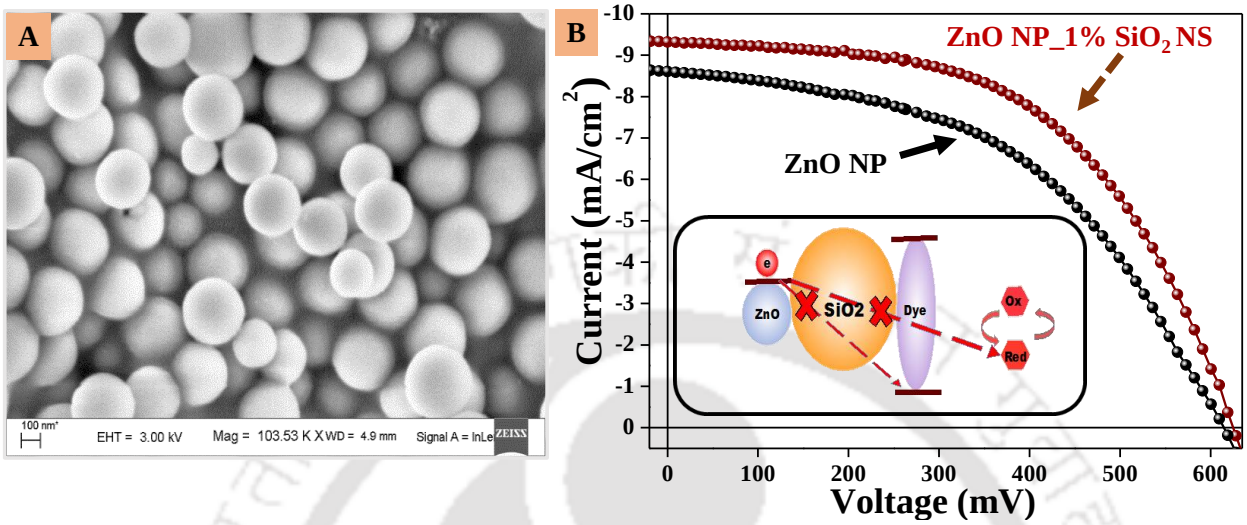

Figure 1. (A) FESEM images of as-synthesized SiO_2 nanospheres **(B)** J-V curves for the bare ZnO NP and ZS_1 device, Inset to trace B depicts schematic representation of inhibited electron interception at ZnO/dye/electrolyte interface **[*Phys. Chem. Chem. Phys.*, 2016, *18*, 27818]**

This chapter presents the effect of submicron sized insulating silica nanospheres (SiO_2 NS) in a binary hybrid photoanode with zinc oxide nanoparticle. The synthesis of the materials were achieved by easy and cost effective synthetic routes. Optimized photoanode with 1% SiO_2 NS achieved a ~ 22% enhancement in power conversion efficiency (PCE) compared to the reference device. A systematic investigation revealed the bifunctional nature of the silica nanospheres in enhancing the device efficacy compared to its bare counterpart. Enhanced performance of the proposed solar cell can be ascribed to following key factors – i) Better light harvesting efficiency of the photoanode by optical confinement resulting in increased propagation length of incident light by multiple internal reflections furnished by SiO_2 NS ii) Minimum photoinduced electron interception to the redox shuttle (I^-/I_3^-) at the working electrode/electrolyte interfaces in presence of insulating SiO_2 NS. Higher recombination resistance (R_{ct}) in case of 1wt% composite indicates that SiO_2 NS serves as a partial energy barrier layer retarding the interfacial recombination (back transfer) of photo-generated electrons at working electrode/ electrolyte interface thus increasing the device efficiency. Figure **1** represents morphological features of as synthesized SiO_2 NS and the J-V curve for the bare as well as best performing photoanode.

Chapter 4: **Nanocube assembled $SrTiO_3$ in enhancing the photovoltaic properties through its energy barrier and light scattering effects**

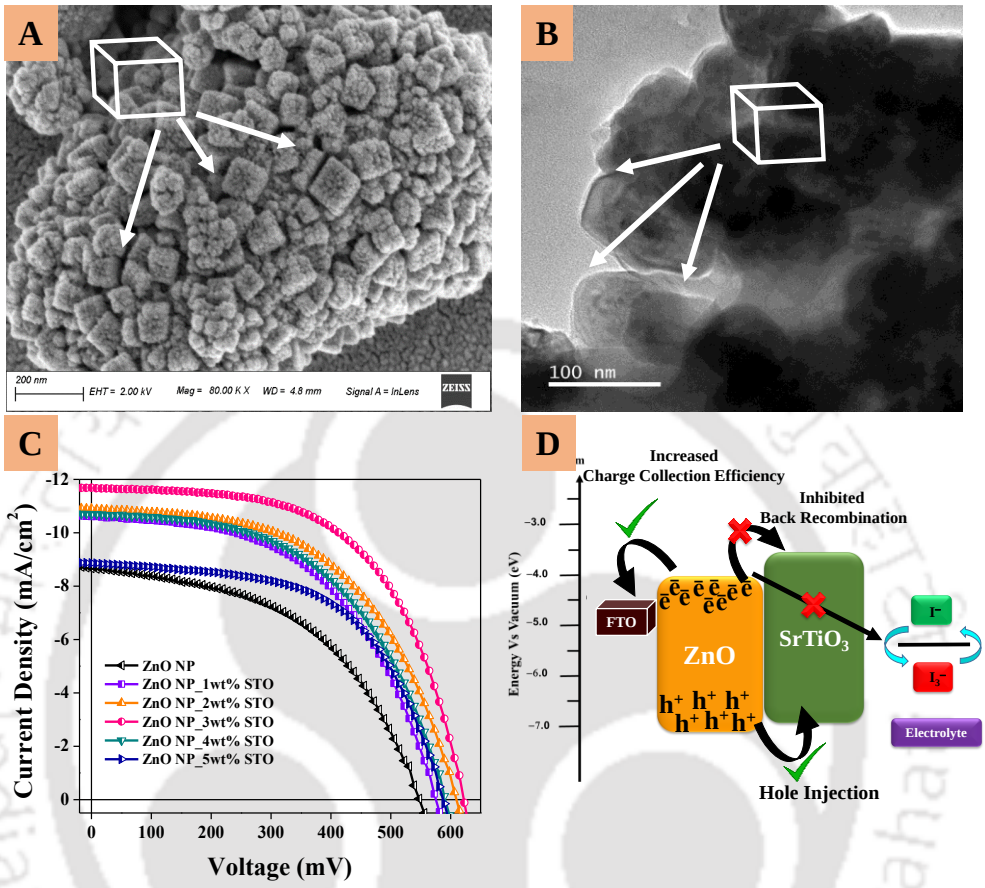

Figure 2. (A) FESEM images of as synthesized STO NCMS **(B)** Magnified TEM image of STO NCMS **(C)** *J-V* curves of the fabricated photoanodes **(D)** Shematic representation the charge transfer processes occurring in the composite devices **[*J Phys. Chem. C*, 2018, *122*, 16550]**

This chapter presents utilization of perovskite ternary oxide, $SrTiO_3$ microstructure formed by self-assembly of nanocubes (STO NCMS) in the photoanodic section in composite with zinc oxide nanoparticle. Synthesis of STO NCMS was achieved by a two-step hydrothermal route in highly alkaline medium of pH ~12. A **~ 2-fold increase** in the power conversion efficiency (PCE, η) is displayed by ZnO NP_STO NCMS [for an optimized 3% STO NCMS] composite photoanode device compared to pristine device. Improved performance of photoanode with hybrid composite scaffold can be accredited to the boosted optical response in conjunction with impeded reverse tunneling probability of STO NCMS containing photoanode. Enhanced light harvesting through increased interaction of sensitizer with incident light is achieved via optical confinement of incident light by multiple reflections generated from mirror like facets of $SrTiO_3$ nanocubes as

well as an enhanced light scattering effects from individual entity. IPCE analysis revealed a better absorption of low energy photons that in turn resulted in an enhanced solar to electricity generation for an optimized ratio of STO NCMS. An effective photoinduced charge separation with a uniquely aligned band structure between ZnO and STO NCMS creates thermodynamic driving force and improves electron transfer ability from the LUMO of dye to CB of $SrTiO_3$ to that of ZnO which increases charge injection efficiency from excited state of dye as well as holes in the valence band of ZnO can migrates to the VB of STO NCMS results in an increased charge collection efficiency of the devices. Moreover, a ~ 200 meV negative CB position of STO acts as a partial energy barrier to the photo-injected electrons thus reducing the back recombination. Morphological features as well as photovoltaic characteristics along with schematic showing the plausible mechanism of electron transfer is depicted in figure **2**.

Chapter 5: **High quality mirror-like nano cuboidal CeO_2 coupled with reduced Graphene Oxide for superior light harnessing and charge transfer dynamics**

This chapter demonstrates exploration of a ternary hybrid composite utilizing nano-cuboidal CeO_2 (CeO_2 NC) and 2D-*reduced* graphene oxide (2D-RGO) sheets in conjunction with ZnO nanoparticle and introduced in the photoanodic segment. Synthesis of CeO_2 NC was achieved via hydrothermal route whereas, RGO was synthesized by an oxidation followed by reduction process. Firstly, Graphene oxide (GO) was prepared utilizing graphite as a precursor. Reduced graphene oxide was synthesized by chemical reduction of graphene oxide. A nearby ~ 6% power conversion efficiency (PCE) has been achieved for photoanode with optimized CeO_2 NC concentration loaded with 1wt% RGO. A ~30% increase in the short-circuit current density (J_{sc}), ~14 % in open circuit voltage (V_{oc}) as compared to bare photoanode is accredited to combination of enhanced light harnessing efficiency as well as better transport of photo-induced charges in the hybrid device. Nano-cuboidal CeO_2 owing to its size and mirror like facets provides a better light harvesting by photoanode through multiple interactions of incident photon with the absorber as well as acts as a partial energy barrier for photoinduced electron interception due to higher conduction band edge position, at the working electrode/electrolyte interfaces. Whereas, an effective photoinduced charge separation with a uniquely aligned band structure between ZnO, CeO_2 via 2D RGO sheets resulted in an increased charge collection efficiency of the devices. A substantial increase in the FF of the devices is resulted from better charge separation, injection as

well as transport offered by RGO sheets having very high electron mobility. Phase characterization, morphological features of as synthesized materials as well as device characteristics are shown in figure **(3)**, **(4)** and **(5)**.

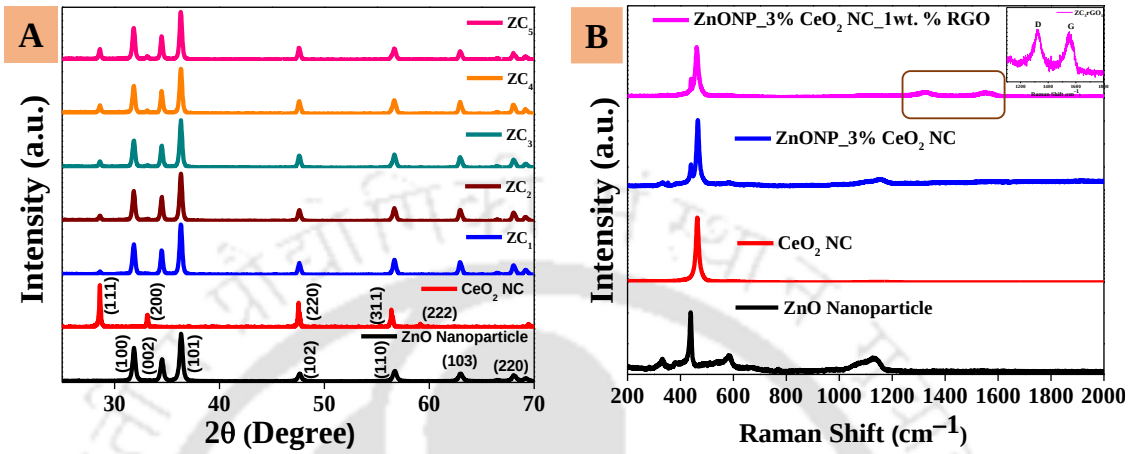

Figure 3. (A) PXRD spectra of ZnO NP, CeO_2 NC, and composites ZCx (x=1-5) **(B)** Raman Spectra of ZnO NP, CeO_2NC, ZC3 and ZC_3RGO_1. (Manuscript Submitted)

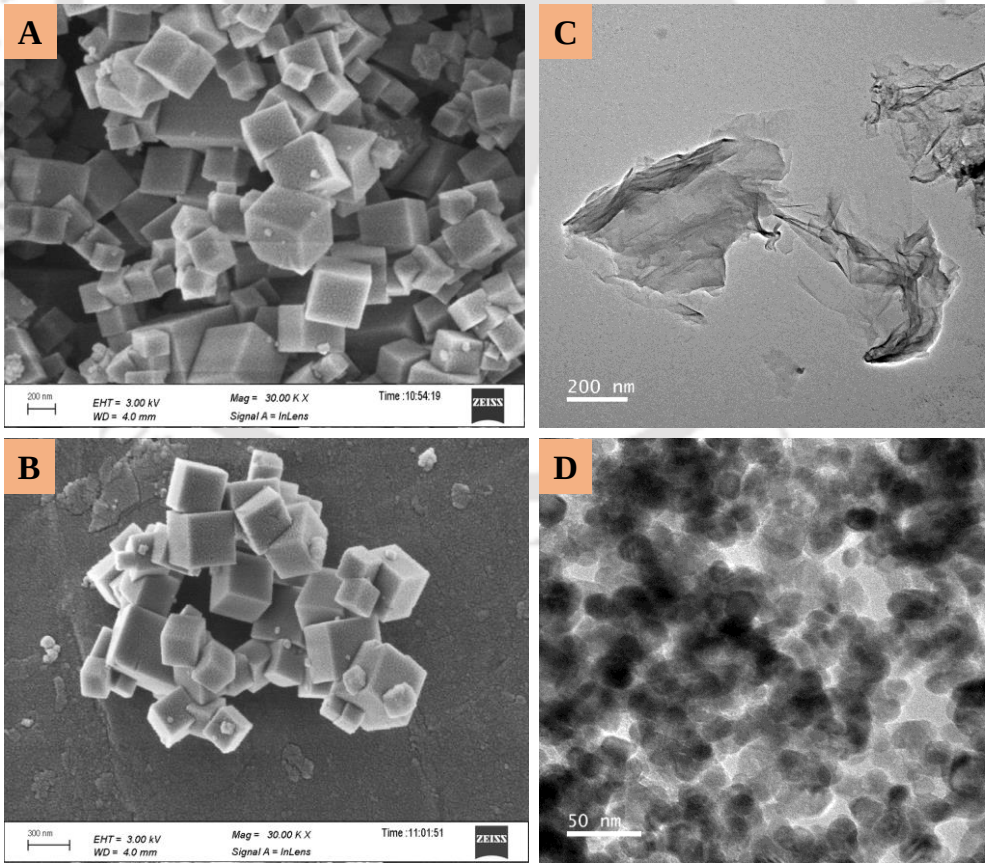

Figure 4. (A) FESEM and **(B)** Magnified FESEM images of CeO_2NC **(C)** TEM image of RGO and **(D)** TEM image of ZnO NP (Manuscript Submitted)

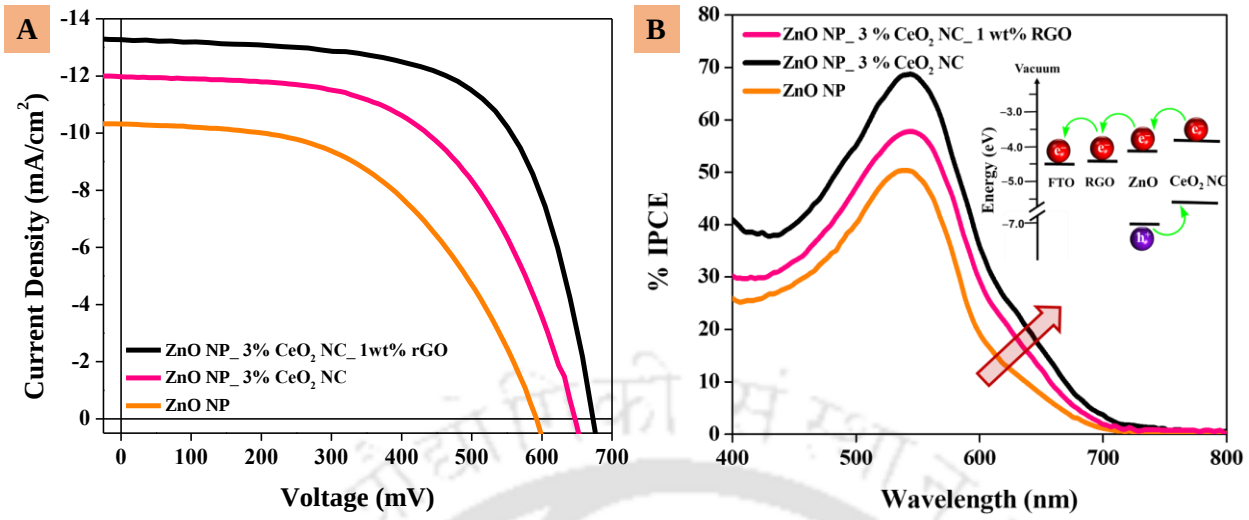

Figure 5. (A) J-V curve **(B)** IPCE plot of fabricated ZnO NP, ZC_3, ZC_3RGO_1 photoanode based devices (Manuscript Submitted)

Chapter 6: Nano-amassed mesoporous zinc oxide hollow microspheres as synergy boosters for efficient energy harvesting in SnO_2 based dye- sensitized solar cell

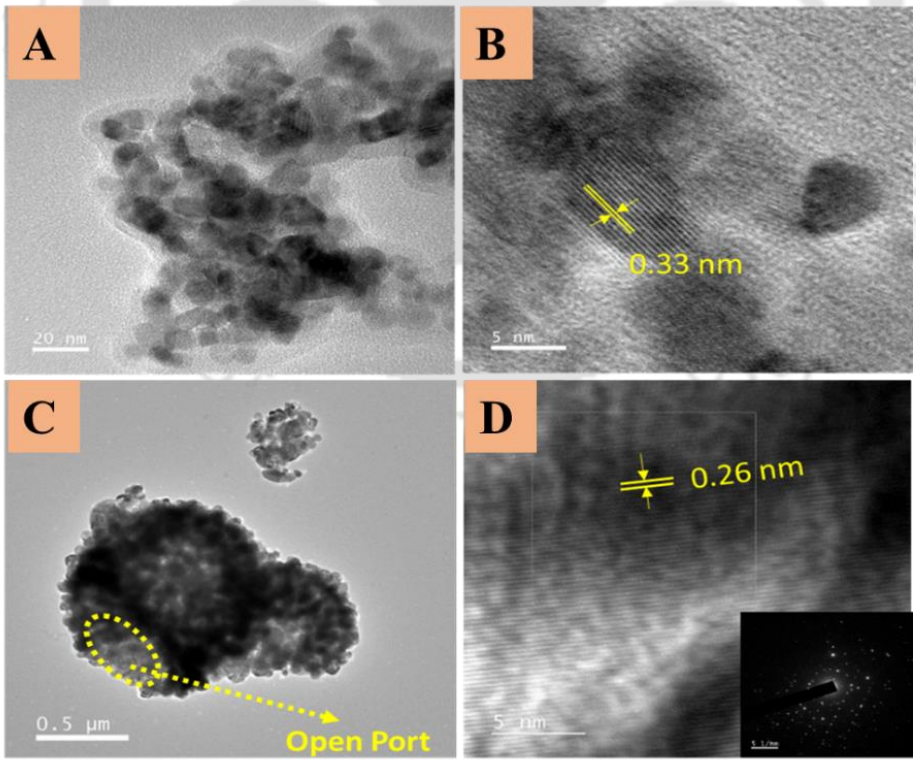

Figure 6. TEM and HRTEM images of **(A)** SnO_2 NP and **(B)** ZnO HS **[*ACS Omega, 2018, 3,* 14482]**

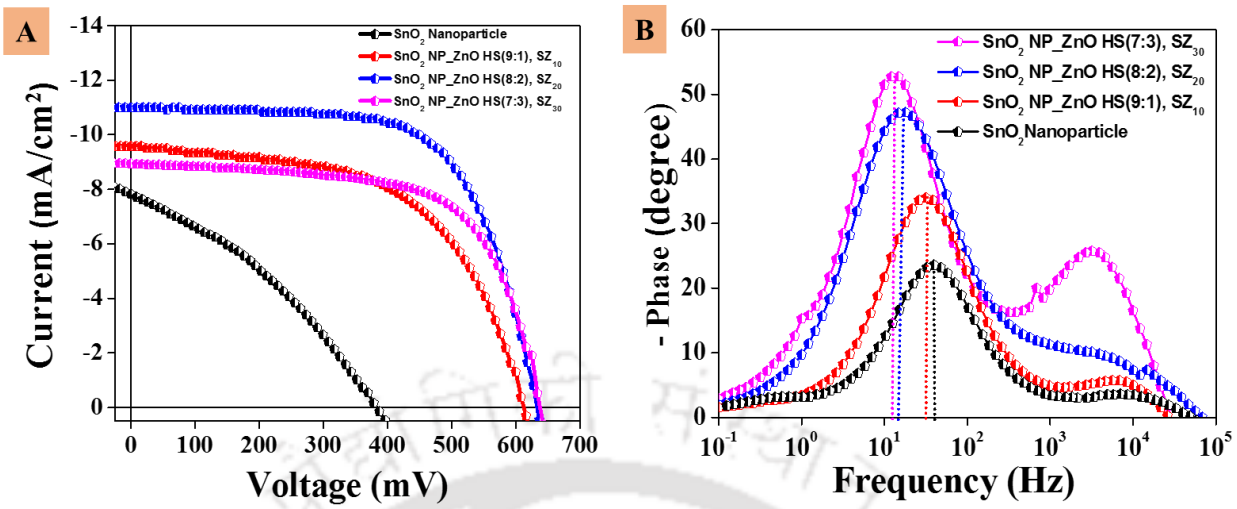

Figure 7. (A) *J-V* curve **(B)** EIS (Bode Phase Plot) plot of SnO_2 NP and SZx (x=10, 20, 30%) photoanode based devices **[*ACS Omega, 2018, 3,* 14482]**

This chapter demonstrates a practical strategy to boost efficiency in sparsely studied SnO_2 nanoparticle based photoanode by using nano-amassed micron sized mesoporous zinc oxide hollow spheres (*meso*-ZnO HS). SnO_2, one of the promising material suffers in terms of efficacy due to its inherent issues such as faster electron recombination and low fill factors and been a dire issue to deal with. A binary hybrid photoanode utilizing nano-amassed micron sized mesoporous zinc oxide hollow spheres (*meso*-ZnO HS) in conjunction with SnO_2 nanoparticle (NP), i.e. SnO_2 NP_ ZnO HS [for an optimized weight ratio (8:2)] displayed a near ~ 4–fold increase in the power conversion efficiency as compared to pristine SnO_2 NP device. *Meso*-ZnO HS are synthesized by an Ostwald ripening process in reflux conditions using Zn $(NO_3)_2.6H_2O$ and PEG 200. Enhanced device performances in case of composite based photoanodes [SnO_2 NP_ ZnO HS] have been explained on the basis of better light harvesting capability of the composite photoanode as well as impeded reverse tunneling probability of photo-induced electron at semiconductor/dye/electrolyte interface. Around ~100% increase in the fill factors in case of composite based devices is due to facilitated diffusion of electrolyte through the pores of *meso*-ZnO HS, thus increasing the regeneration probability of oxidized dye. Moreover, a type II band alignment formed between well matched band positions of SnO_2 and ZnO heterostructures results in a charge carrier separation (electrons on SnO_2 and holes on ZnO) leads to reduced recombination and thus increases charge carrier lifetimes. Phase characterization, morphological features of as synthesized materials as well as device characteristics are shown in figure (6) and (7).

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