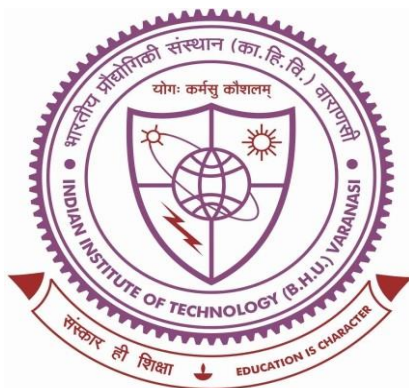


Fabrication and Characterization of Some ZnO Colloidal Quantum Dots and Organic Semiconductor Heterojunction Based Ultraviolet-visible Photodetectors



Thesis submitted in partial fulfillment for the
Award of Degree

Doctor of Philosophy

By

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Date: 19/07/2023



(Abhinav Pratap Singh)

**Dedicated
To
My Beloved
Parents**

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LIST OF ABBREVIATIONS

Abbreviation	Details
DMSO	Dimethyl sulfoxide
O-D	Zero dimensional
1-D	One dimensional
2-D	Two dimensional
3-D	Three dimensional
ITO	Indium doped tin oxide
PEDOT: PSS	Poly (3, 4-ethylene dioxythiophene): polystyrene sulfonate
DMF	Dimethylformamide
EQE	External quantum efficiency
DI	Deionized
ZnO	Zinc oxide
CH ₃ NH ₃ PbI ₃	Methylammonium lead iodide
MoO ₃	Molybdenum trioxide
EHPs	Electron-hole pairs
ETL	Electron transport layer
HTL	Hole transport layer
FTO	Fluorine doped tin oxide
XRD	X-Ray diffraction
SEM	Scanning electron microscopy
UV-Vis	Ultraviolet-visible spectroscopy
PL	Photoluminescence spectroscopy
VB	Valence band
CB	Conduction band

LIST OF SYMBOLS

Symbol	Details
λ	Wavelength
θ	Diffraction angle
T	Transmittance
A	Absorbance
τ_r	Rise time
τ_F	Fall time
R_λ	Responsivity
J	Photocurrent density
I_{light}	Current under light illumination
I_{dark}	Current under dark condition
A	Effective exposed irradiation area
P_d	Optical power
D	Detectivity
RA	Resistance–area product
K	Boltzmann constant
T	Temperature
q	Electronic charge
ϵ	Effective dielectric constant
N_d	Donor concentration
V_{bi}	Built-in potential voltage
W	Width of the depletion region
V	Applied Voltage
α	Absorption coefficient
$P_{\text{opt}}(\lambda)$	Optical power density

Preface

The primarily objective of this thesis is to investigate the electrical and optical performances of some ZnO colloidal quantum dots (CQDs) and organic semiconductor based inorganic-organic heterostructures for ultraviolet-visible (UV-vis) photodetection applications. TIPS-Pentacene (a small-molecule organic semiconductor) and F8BT (polymer-based organic semiconductors) have been explored as p-type organic semiconductors while ZnO CQDs have been utilized as n-type material in the heterostructures investigated in this thesis. The inherent traps/defects in ZnO CQDs have been explored to create a photomultiplication effect in such photodetectors to enhance the external quantum efficiency (EQE) beyond 100%. The present thesis consists of SIX chapters which are briefly outlined in the following:

Chapter 1 covers the basic introduction to photodetectors, performance metrics, materials and methods, state-of-the-art literature review of organic photodetectors, photomultiplication-based photodetectors, and a review of self-powered photodetectors. This chapter also includes the motivation, problem statement, and objective of the thesis.

Chapter 2 investigates a ZnO CQDs/TIPS-Pentacene based inorganic-organic heterostructure based UV photodetector. This chapter covers the basic experimental steps, absorbance and photoluminescence (PL) studies of the materials followed by electrical and optical characterization to extract performance parameters like responsivity, external quantum efficiency, detectivity, and time response. The measurement of the photoresponse of the device was carried out using a monochromatic light source in the range of 300–700 nm. Upon illumination with UV light on the device under -1 V reverse bias, the photodetector

exhibited the maximum responsivity of ~ 59.15 A/W and detectivity of $\sim 7.01 \times 10^{13}$ cmHz^{1/2}/W.

Chapter 3 is devoted to the enhance the performance enhancement of the ZnO CQDs/TIPS-Pentacene based heterostructure discussed in Chapter-2 by using a thin MoO_x layer as hole transport layer (HTL). The MoO_x layer was used to prevent the electron injection into the device to reduce the recombination of photogenerated carriers and hence the dark current of the device. The device showed a broad photoresponse in the UV-visible region with the maximum responsivity of 217.31 A/W, EQE of $\sim 69811\%$ and detectivity of $\sim 6.79 \times 10^{12}$ cmHz^{1/2}/W under the incident light intensity of ~ 64.8 $\mu\text{W}/\text{cm}^2$ at 386 nm in the UV region and the maximum responsivity of ~ 57.34 A/W, EQE of $\sim 11111.3\%$ and detectivity of $\sim 1.79 \times 10^{12}$ cmHz^{1/2}/W under the light intensity of 48.8 $\mu\text{W}/\text{cm}^2$ in the visible region at 640 nm under -1 V reverse bias operation.

Chapter 4 explored an inorganic-organic heterostructure based UV-visible photodetector using ZnO CQDs as inorganic material and F8BT polymer as organic semiconductor in the heterostructure. Two vertical device structures have been studied, namely: ITO/ ZnO CQDs/ F8BT/ Ag (Device-1) and ITO/ ZnO CQDs/F8BT/MoO_x/ Ag (Device-2). In Device-2, the additional MoO_x layer is used to act as the HTL to enhance the performance of Device-1 as investigated in Chapter-3. The chapter includes detailed experimental steps followed by absorbance and photoluminescence studies of the various thin films used in the proposed devices. The Device-1 (without the MoO_x layer) showed the maximum responsivity of 24 A/W, while the Device-2 (with the MoO_x layer) showed the maximum responsivity of 44 A/W under a light intensity of 25 $\mu\text{W}/\text{cm}^2$ of 385 nm at -1 V reverse bias operation. The Device-2 (with the MoO_x layer) also exhibited a self-powered characteristic with the

maximum responsivity of ~ 59 mA/W and external quantum efficiency of 18.98 % under zero bias operation.

Chapter 5 reports the fabrication and characterization of ZnO CQD/ TIPS-Pentacene:F8BT heterostructure based UV-visible photodetector with and without MoOx HTL. The chapter covers the experimental details and optical characterization of the thin films used in the device. The optical response of the proposed device has been measured over the wavelength range of 350-700 nm at an incident radiation intensity of $17.43 \mu\text{W}/\text{cm}^2$ under a reverse bias of -1 V. The maximum responsivity of the device is shown to increase from 29.60 A/W to 70.20 A/W at 350 nm by using the MoOx HTL layer. In the visible region at 470 nm, the maximum responsivity was improved from 13.68 A/W to 40.92 A/W.

Chapter 6 is used to summarize the major observations of the present thesis. The possible extension of the ideas and concepts explored in present works for future studies is also briefly outlined in this chapter.