CHAPTER 7
SURFACE MODIFICATION AND CHARACTERIZATION OF ZnO
NANORODS WITH C₆₀ SHELL LAYER

7.1 INTRODUCTION
Zinc oxide is developing as a unique material for applications in printable and flexible electronics due to its wide band gap semiconductor nature (Voigt et al. 2011). Among the various ZnO nanostructures, 1-D ZnO nanorods have attracted great interest for their immeasurable potential applications in fabricating nano-scale devices. Recently, in material science carbon nano-materials are extensively studied (Schedin et al. 2007, Meyer et al. 2007 and Son et al. 2010) and opening up an innovative research area because of the numerous studies on their incredible electrical properties and diverse potential applications (Son et al. 2012). C₆₀ (fullerene) molecule is considered as the third allotrope of carbon which comprises of 20 hexagonal and 12 pentagonal rings creating a soccer or bucky-ball shape that are held together by weak van der waals interactions wherein all carbon atoms are placed at the nodes of a series of hexagons and pentagons (Guang et al. 2013). In particular, as C₆₀ is an excellent electron acceptor when combined with ZnO, the organic molecules adsorption promises the fine-tuning of electronic properties (Bonifazi et al. 2002). Owing to their exclusive structures and interesting properties, research involving C₆₀ has been increased in the fields of physics, chemistry and material science (Feng et al. 2011). Furthermore, C₆₀ possess wide range of applications in superconductivity (Takeya et al. 2013), organic thin film transistor (Haddon et al. 1995), organic solar cells (Yoo et al. 2004), etc. Huang et al. (2010) reported that infiltration of fullerene as a functional interlayer onto the
ZnO nanorod arrays (NRAs) provides significant improvement in the organic/inorganic hybrid solar cell device performance. Specifically, for excellent potential applications in next-generation nonvolatile memory devices, inorganic nanostructures containing hybrid inorganic/organic composites are now considered as excellent candidates (Son et al. 2010). Moreover, surface modification of inorganic semiconductor nanostructure is useful to increase the charge transport at the inorganic/organic interface in hybrid photovoltaic devices (Chen et al. 2011). Therefore, it is imperative to facilitate the surface coating of 0-D C$_{60}$ shell layer onto the 1-D ZnO NRs in order to obtain surface modified ZnO/C$_{60}$ core/shell composites which provide a path way for tailoring the structural, electrical and optical properties.

In this chapter, surface modification of ZnO NRs with C$_{60}$ shell layer has been formed via simple chemical route to obtain ZnO/C$_{60}$ core/shell–type hybrid NR thin film. The structural, morphological, optical and electrical properties of surface modified films are studied using various characterization techniques.

### 7.2 EXPERIMENTAL METHOD

#### 7.2.1 Synthesis of core ZnO nanorods

A two-step chemical bath deposition method (Yang et al. 2009) has been employed to grow well-aligned ZnO NRs. The detailed description of synthesizing ZnO NRs is given in section 4.2 (chapter 4). The prepared ZnO NRs on glass substrate was used for further formation of C$_{60}$ shell layer.

#### 7.2.2 Synthesis of C$_{60}$ shell layer

The deposition of C$_{60}$ shell layer on to the ZnO NRs has been carried out using spin coating technique (Chen et al. 2011). 0.045g of C$_{60}$ powder purchased from sigma Aldrich with 99.95% purity was dispersed in 3 ml of chlorobenzene [C$_6$H$_5$Cl] and the resultant dispersed solution was spun over the ZnO NRs at the rate of 3000 rpm for 30 seconds. The spin coating process was repeated up to 7 times to accomplish a uniform C$_{60}$ shell layer distribution on the entire surface of ZnO NRs. The transformation of ZnO film surface from white to grey colour indicates the
formation of C$_{60}$ shell layer over ZnO NRs. Figure 7.1 shows a schematic representation of formation of ZnO/C$_{60}$ core/shell NR thin film.

**Figure 7.1** Schematic representation of formation of ZnO/C$_{60}$ core/shell NR thin film

### 7.3 CHARACTERIZATION TECHNIQUES

Microstructural studies have been carried out using X-ray Schimadzu XRD-6000 diffractometer with Cu-K$_\alpha$ radiation recorded in the range 4 to 90°. Fourier transform infrared spectroscopy (FTIR) analysis was carried out using IR prestige-21 Shimadzu Fourier transform infrared spectroscopy. The detailed microstructural properties were analyzed using JEOL JEM 2100 high resolution transmission electron microscope (HRTEM) and surface morphological studies were performed by FEI Quanta FEG 200-high resolution scanning electron microscope (HRSEM) attached with energy dispersive X-ray analysis (EDX). UV-visible-NIR spectra were recorded using JASCO-670 UV/VIS/NIR spectrometer. Room temperature photoluminescence (PL) analysis was performed using a
Fluoromax-4 spectrophotometer. The current to voltage (I-V) measurements were carried out using an automated testing device by National Instruments (NI PXI-1044).

7.4 STRUCTURAL STUDIES

In this section, the structural properties of surface modified ZnO/C₆₀ core/shell NR thin films are discussed. To examine the crystal structure and purity of the prepared samples, XRD analysis was performed in the range of 4 to 90° in steps of 0.1° at a scanning speed of 3°/min. The observed reflections were verified using JCPDS files.

7.4.1 X-ray diffraction analysis of surface modified ZnO/C₆₀ core/shell NRs

![X-ray diffraction patterns](image)

**Figure 7.2** X-ray diffraction patterns of bare ZnO NR and surface modified ZnO/C₆₀ core/shell NR thin films
Figure 7.2 gives the X-ray diffraction patterns for the bare ZnO NRs and surface modified ZnO/C$_{60}$ core/shell ZnO NR thin films. On comparing the XRD pattern of hybrid with the bare ZnO NRs film, both exhibit a sharp and intense diffraction peak at 34.5° corresponding to the (002) plane of ZnO demonstrating the high crystallinity with the preferred c-axis growth orientation of ZnO NRs. There are other weak diffraction peaks centered at 31.7°, 36.4°, 47.6°, 63.0°, 68.0° and 72.7° belonging to (100), (101), (102), (103), (112) and (004) planes respectively of hexagonal wurtzite crystal structure of core ZnO NRs [JCPDS card no. 79-0205]. It is to be noted for the ZnO/C$_{60}$ core/shell structure, the X-ray diffractogram reveals the presence of C$_{60}$ shell layer along with the ZnO NRs which is confirmed by the appearance of four additional diffraction characteristic peaks positioned at 10.8°, 17.7°, 20.7° and 21.7° corresponding to the well matched (111), (220), (311) and (222) reflecting planes respectively of face-centered cubic (fcc) structure of C$_{60}$ [JCPDS card no. PDF #812220].

**7.4.2 FTIR analysis of surface modified ZnO/C$_{60}$ core/shell NRs**

The surface modification of ZnO nanorods with C$_{60}$ has been analyzed by FTIR studies. Figure 7.3 shows FTIR spectrum for bare ZnO and surface modified ZnO/C$_{60}$ core/shell NRs recorded in the wavenumber range from 400 to 4000 cm$^{-1}$. The broad absorption band appearing at 3433 cm$^{-1}$ for bare ZnO is attributed to the O-H stretching vibrations of hydroxyl groups due to the adsorption of water on the surface of ZnO nanorods which is found to slightly shift to lower wavenumber region of 3431 cm$^{-1}$ for ZnO/C$_{60}$ core/shell NRs because of the surface modification of ZnO NRs with C$_{60}$ molecules. The peaks observed between 2300 to 2900 cm$^{-1}$ are assigned to C-H stretching vibration mode of the alkane groups (Krishnan et al. 2009). The two bands located at 1591 and 1421 cm$^{-1}$ in bare ZnO accounting to the asymmetric and symmetric stretching vibrations of carboxyl groups (-COOH) have been shifted to 1618 and 1428 cm$^{-1}$ in ZnO/C$_{60}$ which clearly indicates the chemisorption of C$_{60}$ on the surface of ZnO nanorods by carboxyl groups. The peaks positioned at 1184 and 1024 cm$^{-1}$ correspond to deformation
mode and the stretching vibration of C-O respectively. The appearance of an additional new peak at 525 cm$^{-1}$ in the finger print region (<1000 cm$^{-1}$) belongs to C$_{60}$ (Li et al. 2007) which confirms the successful functionalization of ZnO NRs by C$_{60}$. The peak at 422 cm$^{-1}$ due to the Zn-O stretching vibrations of ZnO nanorods is found to shift to a lower wavenumber region of 420 cm$^{-1}$ for the ZnO/C$_{60}$ core/shell NRs which may be attributed to the surface changes of ZnO NRs.

![FTIR spectrum](image)

**Figure 7.3** FTIR-analysis for bare ZnO NR and surface modified ZnO/C$_{60}$ core/shell NR thin films

7.4.3 HRTEM analysis of surface modified ZnO/C$_{60}$ core/shell NRs

Crystallography and microstructure of the as-synthesized sample is further characterized by HRTEM analysis taken in the dimension ranging from 100 to 21 nm. Figure 7.4 (a-c) show surface modified HRTEM images of ZnO/C$_{60}$ core/shell nanorod. Obviously, adsorption of ~3 nm thickness of C$_{60}$ shell layer has
been established by the appearance of a fine dark band of C\textsubscript{60} wrapping around the ZnO nanorod as shown in figure 7.4 (a). Evidently, figure 7.4 (a)-(c) shows the existence of spherical shaped C\textsubscript{60} bucky-balls of diameter varying from 3 nm onwards decorate (marked by arrows) the surface of ZnO nanorod. The corresponding SAED pattern of ZnO/C\textsubscript{60} core/shell nanorod shown in figure 7.4 (d) represents the monocrystalline ZnO nanorod and polycrystalline C\textsubscript{60} of the core/shell heterostructure.

**Figure 7.4 (a)-(c) Low and high magnification HRTEM images of ZnO/C\textsubscript{60} core/shell nanorod thin film**
7.5 MORPHOLOGICAL STUDIES

In this section, surface morphology of surface modified ZnO/C₆₀ core/shell NRs is studied using HRSEM images taken at a magnification of 40,000x.

7.5.1 HRSEM analysis of surface modified ZnO/C₆₀ core/shell NRs

Figure 7.5 (a) and (b) show the typical top and cross-sectional view HRSEM images of C₆₀ coated vertically aligned ZnO NRs. The measured length and diameter of the ZnO nanorods are found to be in the range of 1.3-1.7 µm and 50-100 nm respectively. The images depict the growth of bigger clusters of agglomerated C₆₀ crystallites which are loaded on the top surface of ZnO NRs. This is again affirmed in the cross-sectional view HRSEM image as shown in figure 7.5 (b), wherein the ZnO NRs are capped by C₆₀ nanocrystals. Compared with HRTEM images, it is difficult to discern the presence of C₆₀ nanocrystals using the low magnified HRSEM images. Figure 7.6 shows EDX analysis of surface modified ZnO/C₆₀ hybrid core/shell structure.

![HRSEM images of top-view (a) and cross-sectional view (b) of ZnO/C₆₀ core/shell NRs](image)

**Figure 7.5** HRSEM images of top-view (a) and cross-sectional view (b) of ZnO/C₆₀ core/shell NRs
The compositional analysis confirmed the presence of elements such as Zn, O, C, Au and Si found in the sample. The EDX spectra contains Si peak which comes from the substrate and the presence of Au peak is due to the gold sputtering of the sample for HRSEM investigation.

![EDX spectra image](image.png)

**Figure 7.6** EDX spectra of surface modified ZnO/C₆₀ core/shell NR thin film

7.6 OPTICAL STUDIES

This section deals with UV-visible and PL emission spectral studies of surface modified ZnO/C₆₀ core/shell NR thin films.

7.6.1 UV-visible analysis of ZnO/C₆₀ core/shell NRs

Figure 7.7 represents UV-visible absorption spectra of bare ZnO and surface modified ZnO/C₆₀ core/shell heterostructure. C₆₀ being a narrow band gap material compared with ZnO, a notable enhancement is observed in the absorption spectrum after the loading of C₆₀ on the surface of ZnO NRs. There are two absorption edges noticed in ZnO/C₆₀ core/shell structure, one is at 402 nm corresponding to bare ZnO nanorod while the other is related to C₆₀ nanocrystals which makes ZnO to extend its absorption capability of light in the visible region (Katsumata et al. 2012). The presence of two distinct absorption edges corresponding to ZnO and C₆₀ reveals the spatial separation of two semiconducting phases (Guerguerian et al. 2011). In addition, it is also noted that the absorption
edge of ZnO in the C\textsubscript{60} loaded film slightly shifts to longer wavelength region, 402 nm (red-shifted) as compared to the absorption edge of bare ZnO (382 nm) which might be favored by the effective adsorption of C\textsubscript{60} resulting in electronic transition between the C\textsubscript{60} shell and the ZnO core. This can be ascribed to the photo-excitation

**Figure 7.7** Room temperature absorption spectra of bare ZnO and surface modified ZnO/C\textsubscript{60} core/shell NRs

**Figure 7.8** Plot of \((ahv)^2\) versus \(hv\) of surface modified ZnO/C\textsubscript{60} core/shell heterostructure NR thin film
of electrons between highest occupied molecular orbital and lowest unoccupied molecular orbital (HOMO-LUMO) levels from C$_{60}$ which are then injected into the conduction band of ZnO (Bonifazi et al. 2002).

Figure 7.8 shows the plot of $(\alpha h \nu)^2$ versus energy $(h \nu)$ of surface modified ZnO/C$_{60}$ core/shell NR thin film and the energy band gap values are determined by extrapolating the linear portion of the curve to meet the energy axis, $(\alpha h \nu)^2 = 0$. According to the literature reported by many researchers using different kinds of techniques, the narrow band gap semiconductor C$_{60}$ has optical energy gap between the HOMO-LUMO (Zhou et al. 1996) levels vary from 1.5 to 2.3 eV (Yang et al. 1987 and Lof et al. 1992). Moreover, the energy band gap value progressively varies for bare C$_{60}$ thin film based on the crystallinity of the film. The optical energy band gap value is close to 1.5 eV for highly crystalline C$_{60}$ films but for highly disordered films it is near 2.3 eV (Bajwa et al. 2003). However, the present work gives two different energy band gap values of 3.05 eV corresponding to bare ZnO and 1.83 eV related to C$_{60}$ which reveals the crystalline nature of C$_{60}$ shell layer.

7.6.2 PL analysis of surface modified ZnO/C$_{60}$ core/shell NRs

Figure 7.9 Room temperature PL-spectra of bare ZnO and surface modified ZnO/C$_{60}$ core/shell NRs

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PL measurements were performed to investigate the optical quality of the prepared samples. Figure 7.9 depicts PL spectra of ZnO NRs before and after deposition of C₆₀ shell layer with the excitation wavelength of 350 nm. The spectra clearly display a strong near-band-edge (NBE) emission peak centered at 380 nm due to the recombination of excitons while there is a broad deep-level yellow emission centered at 574 nm corresponding to trap emissions for both ZnO and surface modified ZnO/C₆₀ core/shell NRs. It is found that the sharp NBE emission is greatly enhanced while there is suppression observed in the defect emission after incorporating C₆₀ shell layer which indicates the surface modification of ZnO nanorods on improving the optical quality of the film. This might be due to the electronic interactions intensely occurring between ZnO core and C₆₀ shell layers. Chen et al. (2011) reported that the visible emission of ZnO is highly dominated by surface defects which are reduced due to the lesser probability of number of transferred electrons to be trapped at the defect states of ZnO nanorod surface upon wrapping with C₆₀ shell layer. Evidently, the existence of C₆₀ layer causes the electron-hole separation and passivates the defect states on ZnO NRs.

**7.7 ELECTRICAL STUDIES**

In order to study the electrical behaviour of the surface modified ZnO/C₆₀ core/shell NRs, current to voltage (I-V) measurements have been recorded under dark and light illumination conditions with an applied voltage varying from -10 to +10 V.

Figure 7.10 shows I-V measurements for bare ZnO and surface modified ZnO/C₆₀-core/shell NR thin film under dark and light illumination. It is observed that both films exhibit ohmic behaviour, which is a basic requirement for a good conductor. The measured electrical resistivity values for the bare ZnO NRs are 2.86 \( \times 10^{-2} \) and 5.43 \( \times 10^{-3} \) \( \Omega \) cm for dark and light illuminations and the corresponding values for surface modified ZnO/C₆₀ core/shell NRs are 9.69\( \times 10^{-2} \) and 2.23 \( \times 10^{-3} \) \( \Omega \) cm. There is a notable decrease in resistivity from dark to illuminated conditions for both bare ZnO and surfaced modified ZnO NRs that reveals the existence of photo-excited charge carriers and enhancement in effective separation of excitons (Chen et
Noticeably, there is a reduction in resistivity under light illumination after incorporating $C_{60}$ shell layer to provide short and continuous pathways for electron transport process (Huang et al. 2010). This result is well supported with the optical absorption spectra (figure 7.7) showing a significant increase in absorption all over the UV and visible region for the film coated with $C_{60}$. Further, this can be validated by the enhancement in PL emission intensity of surface modified ZnO NRs (figure 7.9) to be attributed to the effective exciton separation coupled with reduced surface defect states. This result reveals that $C_{60}$ shell layer improves the electrical property of ZnO NRs towards the application of photosensitive devices.

Figure 7.10 Plot of I-V characteristics of bare ZnO and surface modified ZnO/$C_{60}$-core/shell NRs under dark and light illumination

7.8 CONCLUSIONS

Surface modified ZnO/$C_{60}$ core/shell-type heterostructure has been successfully synthesized on glass substrate using simple chemical route. XRD results reveal the mixed crystal structures of hexagonal ZnO along with the face-centered cubic $C_{60}$. FTIR-studies give evidence for the occurrence of surface modification on ZnO NRs by $C_{60}$. HRTEM images confirm the formation of ZnO/$C_{60}$ core/shell structure while HRSEMs depict the presence of $C_{60}$ loaded on the surface of ZnO NRs. UV-visible absorption spectrum has two distinct absorption edges corresponding to core ZnO and shell $C_{60}$. PL measurements reveal that the coating of $C_{60}$ as shell layer enhances the optical quality of core ZnO NRs.
by increasing the intensity of NBE emission and reducing the surface defect emission. The electrical resistivity of surface modified ZnO NRs by C\textsubscript{60} is significantly reduced under illumination supporting the features of photo-induced charge carrier generation and enhancement in separation of excitons. Hence, ZnO/C\textsubscript{60} core/shell structure is an excellent choice for fabricating organic/inorganic hybrid optoelectronic devices.