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Sagar D. Delekar
Florida State University

Ananta G. Dhodamani
Shivaji University

Krantiveer V. More
Shivaji University

Tukaram D. Dongale
Shivaji University

Rajanish K. Kamat
Shivaji University

See next page for additional authors

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Authors

Sagar D. Delekar, Ananta G. Dhodamani, Krantiveer V. More, Tukaram D. Dongale, Rajanish K. Kamat, Steve Acquah, Naresh S. Dalal, and Dilip K. Panda

Structural and Optical Properties of Nanocrystalline TiO₂ with Multiwalled Carbon Nanotubes and Its Photovoltaic Studies Using Ru(II) Sensitizers

Sagar D. Delekar,^{*,#,\dagger,\|} Ananta G. Dhodamani,^{#,†} Krantiveer V. More,[†] Tukaram D. Dongale,[‡] Rajanish K. Kamat,[§] Steve F. A. Acquah,^{\|} Naresh S. Dalal,^{\|} and Dillip K. Panda^{*,\|,\perp}

[†]Department of Chemistry, Shivaji University, Kolhapur, 416 004 MS, India

[‡]Computational Electronics and Nanoscience Research Laboratory, School of Nanoscience and Biotechnology, Shivaji University, Kolhapur, 416 004 MS, India

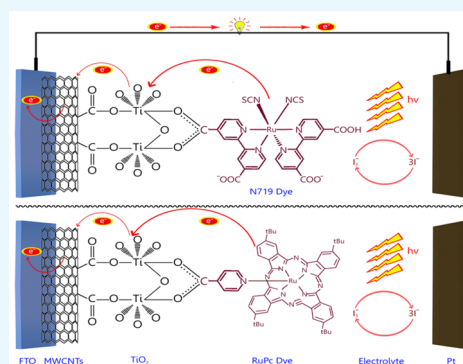
[§]Department of Electronics, Shivaji University, Kolhapur, 416 004 MS, India

^{\|}Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida 30306-4390, United States

^{\perp}Department of Chemistry, Clemson University, Clemson, South Carolina 29634, United States

S Supporting Information

ABSTRACT: In this study, the *in situ* sol–gel method has been deployed to prepare the titanium dioxide/multiwalled carbon nanotubes (TiO₂/MWCNTs) nanocomposite (NCs) powders with varying content of MWCNTs (0.01–1.0 wt %), to construct the dye-sensitized solar cells (DSSCs). First, binder-free NCs were deposited on a transparent-conducting F:SnO₂ (FTO) glass substrate by a doctor-blade technique and then anchored with Ru(II)-based dyes to either N719 or ruthenium phthalocyanine (RuPc). The structural and optical properties and interconnectivity of the materials within the composite are investigated thoroughly by various spectral techniques (XRD, XPS, Raman, FT-IR, and UV–vis), electron microscopy (HRTEM), and BET analysis. The experimental results suggest that the ratio of MWCNTs and TiO₂ in NCs, morphology, and their interconnectivity influenced their structural, optical, and photovoltaic properties significantly. Finally, the photovoltaic performances of the assembled DSSCs with different content of MWCNTs to TiO₂ films anchored with two different dyes were tested under one sun irradiation (100 mW/cm²). The measured current–voltage (*I*_v) curve and incident photon-to-current conversion efficiency (IPCE) spectra of TiO₂/0.1 wt % MWCNTs (T@0.1 C) for N719 dye show three times more power conversion efficiency ($\eta = 6.21\%$) which is opposed to an efficiency ($\eta = 2.07\%$) of T@0.1 C for RuPc dye under the same operating conditions.



INTRODUCTION

Solar energy has become one of the fastest growing industries among all current energy industries. Among the various renewable energy sources, sunlight energy is the largest global energy source and reaches the earth's surface at an average of $4.3 \times 10^{20} \text{ J h}^{-1}$,¹ which is equal to the annual energy demand of today's society. A few generations of solar cell research are already in place for the fabrication of solar cells that convert solar light to electrical power.^{2,3} However, for the last two decades, dye-sensitized solar cells (DSSCs) seem to be one of the most promising, due to their low cost, easy construction and also generate comparable power conversion efficiency to silicon solar cells.⁴ In brief, DSSCs consist of two electrodes, namely, working electrodes (dye-coated semiconductors) and counter electrodes (platinized ITO glass) having an organic-based redox electrolyte (I^-/I_3^-) between these two electrodes. Most of the research has focused on either using a semiconductor TiO₂ or various ruthenium(II) [Ru(II)] based

dyes.⁵ However, the other critical parameters, such as electron density, the mobility of charge carriers, right alignment of energy levels (HOMO and LUMO) of the dye, or redox mediator with respect to valence band and conduction band energy level of the semiconductor, also play a pivotal role in the enhancement of photovoltaic performance of DSSCs.⁶ However, the power conversion efficiency (η) of these devices has reached up to 14.5%.⁷ This efficiency is less as compared to the *S*–*Q* limit (theoretical efficiency of 34% for a single p–n junction)⁸ of DSSCs or nanomaterial-based solar devices (theoretical efficiency up to 66%).⁹ Therefore, the devices with modified TiO₂ (varied in optical and electronic) electrode, anchored with various Ru(II) sensitizers (either N719 or

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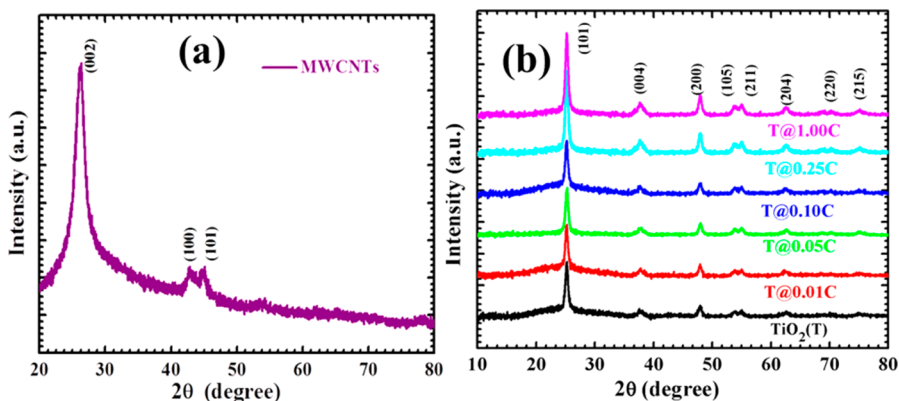


Figure 1. XRD patterns of (a) MWCNTs and (b) bare TiO₂ NPs and TiO₂/MWCNTs NCs with varying content of MWCNTs from 0.01 to 1.0 wt %.

RuPc), would benefit from harvesting more photons from a broad range of the solar spectrum.

Various strategic synthetic routes have been employed, such as doping,¹⁰ supported with metal/metal oxides,¹¹ or composites,¹² to tune the optical, electrical, porosity, and structure-induced morphology of TiO₂; however, importance has been placed on preparing the visible active composites of TiO₂ nanoparticles (NPs) with highly conducting MWCNTs.¹³ TiO₂-MWCNTs NCs research has focused more on design of the electrode for solar energy harvesting materials. The reported synthesis of TiO₂/MWCNTs NCs requires high temperature, expensive chemicals, and materials, and moreover, their nonuniform morphology lowers the performance as working electrode materials. Earlier, Wang et al. synthesized TiO₂/MWCNTs nanohybrids by a single-step laser pyrolysis technique via both *in situ* and *ex situ* ways. However, DSSC efficiencies comprised of these electrodes were limited to only 3.9% and 3.3%.¹⁴ Moreover, the pyrolysis techniques always require state-of-the-art advanced and expensive equipment which is not desirable for photovoltaic technology.¹⁵ Mahmood et al. reported the DSSC efficiency of 5.25% using 0.06 wt % MWCNTs along with commercially purchased TiO₂ paste. These photoelectrodes were prepared by mixing MWCNTs in ethanol with the TiO₂ paste using the sonochemical method.¹⁶ However, MWCNTs not uniformly decorated with TiO₂ particles by this technique were confirmed by TEM analysis. The use of only bare MWCNTs always retards the electron transport between the semiconducting photoelectrode to the counter electrode, overall decreasing the power conversion efficiency of the cells. A high-temperature hydrothermal synthesis of TiO₂/MWCNTs NCs was also reported and resulted in the device efficiency of up to 7.37%, which is higher than that of bare TiO₂ NPs as well as Degussa P25 NPs.¹⁷ The 5 wt % MWCNTs content composites of TiO₂/MWCNTs thin films prepared by an electrospinning technique reported a greater efficiency.¹⁸ The agglomeration is the key problem of this kind of TiO₂/MWCNTs NCs. These NCs also absorb the incident photons actively which retard the electron–hole separation and lower the photovoltaic performance.¹⁹ Also, the electrospinning technique always produces the irregular and nonuniform morphology structure within the NCs which often results in low power energy conversion efficiencies.

Ru(II)-based sensitizers have played a significant role in the development of the solar cells as a chromophore. The efficiency of the DSSCs could be improved significantly if these dyes have absorption in the range of visible to NIR of the solar

spectrum.²⁰ Researchers have studied various chromophores including metal complexes and organic-based dyes. Among all dyes, Ru(II) polypyridine-based sensitizers, mainly black dye, N3, and N719, are the better chromophores for DSSCs due to their promising chemical and photochemical stability along with enhanced photovoltaic performance.²¹ Similarly, the RuPc dye is also used as an alternative dye for DSSCs due to its analogues to N719 dye's structure, chemical and photochemical stability, and high molar extinction coefficient. Indeed, this intrinsic nature of RuPc dye promotes harvesting of more photons in the entire range of the visible to NIR solar spectrum. Also, the suitable electrochemical redox property of RuPc is utilized as a promising dye to anchor semiconducting metal oxides (TiO₂) for other applications.²²

In this work, we report the synthesis of TiO₂/MWCNTs NCs with varying content of MWCNTs by *in situ* sol–gel method, and then these materials are well characterized by various spectroscopies (XRD, XPS, UV–vis, PL, FT-IR, and Raman), microscopy techniques (HRTEM), and BET measurements for knowing their structural, morphological, and optical properties. Thereafter, these materials are deposited on FTO glass substrates by a doctor blade technique to form the photoelectrodes. Finally, the photovoltaic performances of the assembled sandwiched devices made of a different composite of TiO₂/MWCNTs are measured (*IV* and IPCE) under one sun condition (100 mW/cm²) and compared with two different dyes (N719 and RuPc).

RESULTS AND DISCUSSION

The thermal stability and existence of MWCNTs in the NC samples were studied by using thermogravimetric analysis (TGA) and illustrated in the Supporting Information (Figure S1, SI). The crystal structure of the pure phase of the materials (MWCNTs, bare TiO₂ NPs, and TiO₂/MWCNTs NCs) was characterized by using a Powder X-ray diffraction (XRD) technique. XRD pattern of MWCNTs (Figure 1(a)) shows a sharp peak at 26.7° corresponding to a (002) reflection, confirming the presence of elemental carbon (JCPDS No. 41-1487). XRD patterns of TiO₂ and different TiO₂/MWCNTs NCs are presented in Figure 1(b). The various peaks observed at ~25.21 (101), ~37.63 (004), ~47.90 (200), ~53.89 (105), ~55.03 (211), ~62.57 (204), ~69.98 (220), and ~74.93 (215) are the characteristic peaks of anatase TiO₂ (JCPDS No. 21-1272). The sharp, intense peaks of the samples reveal the crystalline nature with crystallite size in the range between 15

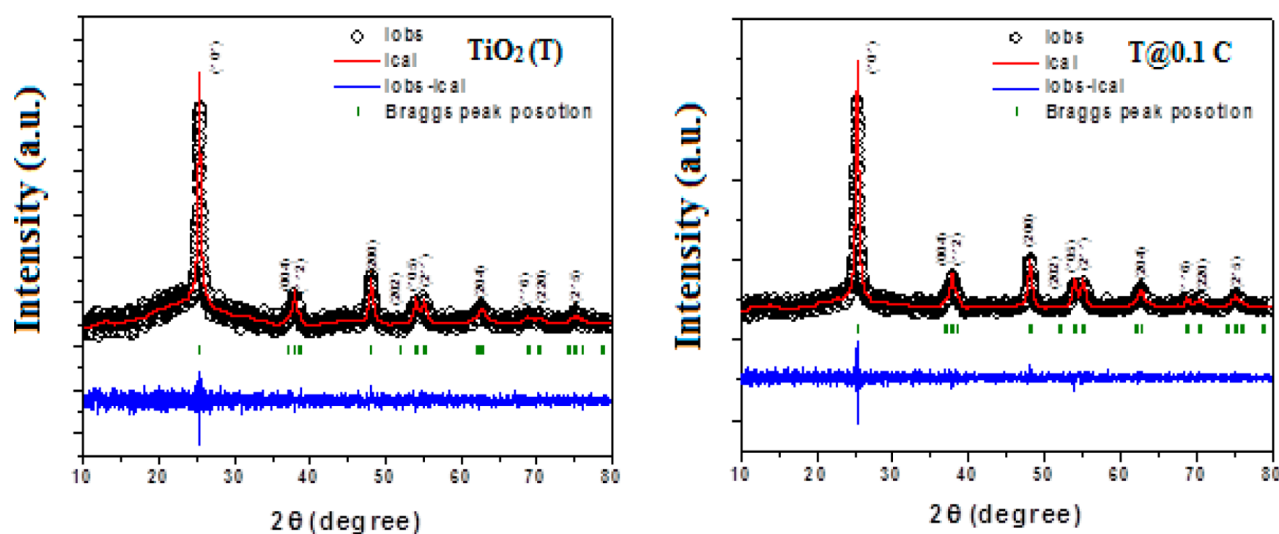


Figure 2. XRD Rietveld refined patterns of (a) bare TiO₂ NPs and (b) T@0.1C NCs.

Table 1. Rietveld Refinement Factors of Bare TiO₂ and TiO₂/MWCNTs NCs with Varying Composition of MWCNTs

Rietveld refinement factors	samples					
	TiO ₂ (T)	T@0.01 C	T@0.05 C	T@0.10 C	T@0.25 C	T@1.00 C
χ^2	1.53	1.59	1.24	1.26	1.60	1.48
R_B (%)	3.65	4.15	1.74	4.62	4.06	3.20
R_F (%)	3.43	4.69	1.72	3.60	4.09	4.62
R_{wp}	29.8	34.4	26.12	34.2	33.5	22.1
R_{exp}	24.1	27.2	21.13	27.1	26.4	18.1
D (nm)	17	18	20	21	22	24
$a = b$ (Å)	3.7880	3.7878	3.7874	3.7854	3.7851	3.7871
c (Å)	9.5025	9.5178	9.5191	9.5097	9.5096	9.5198
V (Å ³)	136.35	136.55	136.54	136.21	136.20	136.51
ρ (g/cm ³)	4.554	4.488	4.505	4.273	4.338	4.475
O position (z)	0.2004	0.2005	0.1993	0.2033	0.1993	0.2003

and 19 nm. The structural cell parameters of the samples are calculated and presented (Table S1, SI). The expected peak position at 26.17 (002) reflection for MWCNTs did not appear in the TiO₂/MWCNTs NCs because of either a tiny amount present in the composition or shielding by the most intense peak of anatase TiO₂ appearing at \sim 25.21 (101).²³ As the content of MWCNTs increases in composite, a small change is observed in the peak positions with a definitive increase in the intensity of characteristic peaks of TiO₂. The change in the peak positions of samples is reflected through the various cell parameters, crystallite size, and lattice strain,²⁴ while the shifts in the intensity of the peaks are justified through the lattice sites of ions present in the TiO₂ lattice (Table S1, SI).²⁵

The quantitative studies related to structural properties were further confirmed by the Rietveld refinement method using the Fullprof 2000 software package. Rietveld refined XRD patterns of the bare TiO₂ NPs and T@0.1C NCs are shown in Figure 2(a,b), and the remaining patterns are also shown in the Supporting Information (Figures S3, S4, S5, and S6, SI).

The lattice reflections such as (101), (004), (112), (200), (202), (105), (211), (204), (116), (220), and (215) in the Rietveld refined XRD patterns confirm the formation of the tetragonal anatase crystal structure. In the refinement, the oxygen positions (x , y , z) have been considered as free parameters, and fractional atomic positions have been taken as fixed. Other parameters such as lattice, temperature,

occupancies, scale factors, and shape parameters have also been considered as free parameters. The quality of the Rietveld refinement quantified by the corresponding figures of merit, viz., R_{wp} , the goodness of fit (χ^2), and pseudo-Voigt function, corrected the background of the pattern.

The atomic coordinates and occupancies of different atoms of the different samples are also presented (Table S2, SI). In the entire refined patterns, the value of “goodness of fit (χ^2)” lies in the range of 1–1.5; this indicates well the extent of fitting. (The Rietveld refined factors such as χ^2 , R_{wp} , R_{exp} , R_B , R_F , etc. of all samples are summarized in Table 1.) The values of the various R factors are slightly higher, which may be due to the nanocrystalline nature of the samples and also could be assigned to the larger signal-to-noise ratio.²⁶ Based on these Rietveld refinements, the average crystallite sizes (D) have been calculated using the Scherrer formula, which is observed from 17 to 24 nm. The increase in crystallite size, as well as little change related to lattice parameters of the samples, is observed with increasing composition of MWCNTs in the TiO₂ host lattice.

Raman spectra of the bare TiO₂ NPs, MWCNTs only, and representative T@0.1 C NCs are shown in Figure 3(a). Raman spectrum of TiO₂ NPs shows the characteristic peaks at 144.69, 398.4, 516.78, and 640.92 cm⁻¹ corresponding to the E_g (1), B_{1g}, A_{1g}, and E_g (2) modes of vibrations, respectively.

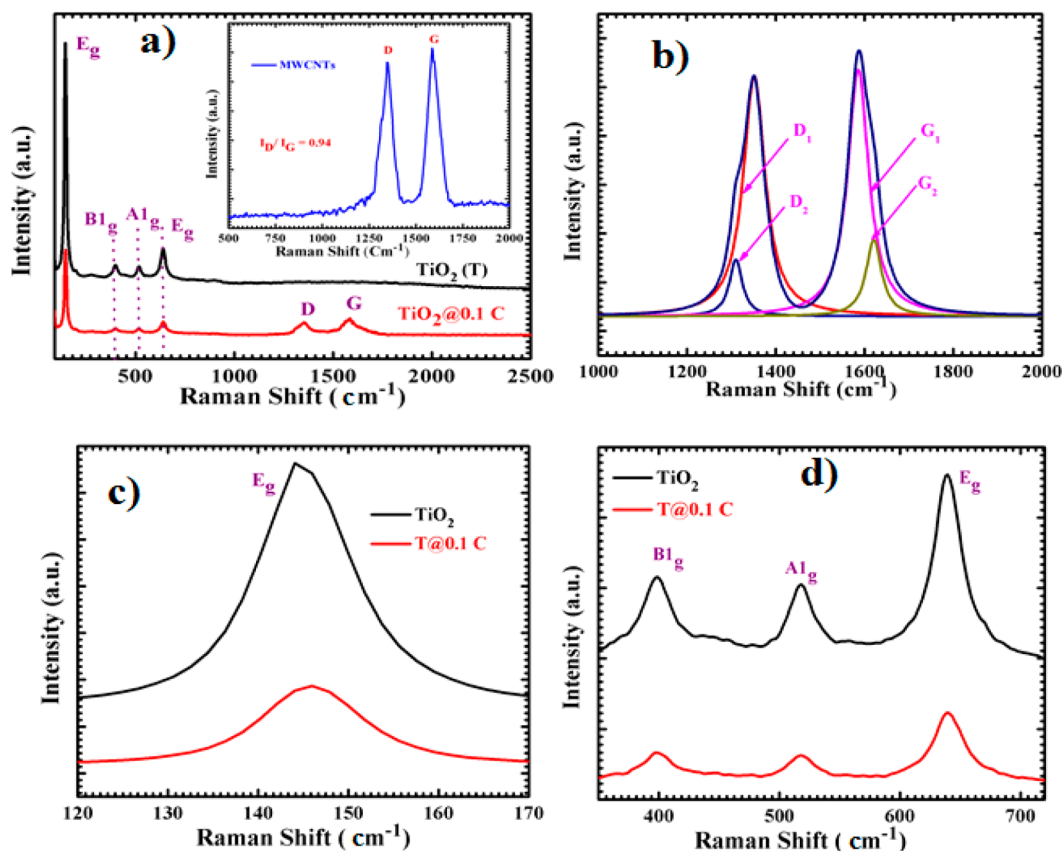


Figure 3. Raman spectra of bare TiO_2 NPs, T@0.1C NCs, and MWCNTs (inset).

These peaks confirm the presence of the anatase phase only, which is in good agreement with the XRD results.²⁷ Raman spectrum of MWCNTs is shown in the inset, which shows two bands, namely, the D band and G band. The D band is an indicative disorder in the graphitic structure at 1346.10 cm^{-1} due to the disorder induced by sp^3 hybridization, whereas the G band (characteristic ordered graphitic structure) at 1585.01 cm^{-1} corresponds to ordered sp^2 hybridization of MWCNTs. The intensity ratio (I_D/I_G) for the functionalized MWCNTs also reveals the presence of acidic functional moieties on the surface of MWCNTs with the conversion of the carbon atoms from sp^2 to sp^3 hybridization. Raman spectrum of functionalized MWCNTs with fitting results (Figure 3b) show graphitizable carbon activated by acidic functional moieties.²⁸ Raman spectrum of a representative T@0.1 C NCs shows all the characteristic peaks of anatase TiO_2 along with D (1350.96 cm^{-1}) and G (1582.32 cm^{-1}) bands of MWCNTs. It emphatically reveals the existence of MWCNTs composition in the NCs.²⁹ The decrease in the peak intensity, with little shifting in the peak positions of all Raman bands, for NCs, is shown in Figure 3 (c and d). It is usually due to the increase in the crystallite size with an increase in the MWCNTs content in the TiO_2 host lattice.

Transmission electron microscopy (TEM), high-resolution TEM (HR-TEM) with selected area electron diffraction (SAED) patterns of MWCNTs, bare TiO_2 NPs and T@0.1 C NCs are shown in Figure 4 (a to i). TEM image (Figure 4(a)) of MWCNTs shows the cylindrical tubes having an average outer diameter in the range between 20 and 25 nm and a few micrometers in length. From HRTEM image (Figure 4(b)), the distance between the two successive inner layers of

MWCNTs is around 0.33 nm, while the diameter between the two outermost shells is 23 nm. SAED pattern (Figure 4(c)) shows the bright ring patterns, which correctly match to the spacing of the (002), (100), and (006) reflections. Figure 4(d,e,f) shows TEM, HRTEM, and SAED patterns of the bare TiO_2 NPs. A TEM image shows the spherical nanostructures having a mean particle diameter of 15–20 nm, while spacing for the (101) lattice fringes is 0.352 nm. SAED pattern indicates excellent crystallinity due to a clear ring structure with lattice points that directly match the anatase phase of TiO_2 . Figure 4(g,h,i) shows TEM, HRTEM, and SAED patterns of representative T@0.1 C NCs. TEM image shows the spherical nanostructures of the TiO_2 NPs directly anchored on the surface of MWCNTs, and no bare MWCNTs is observed because of the high wall anchoring as well as density of TiO_2 NPs.

HRTEM micrograph shows that the clear fringes precisely match to the spacing of the (101) reflection of TiO_2 NPs. However, uncleaned fringes of MWCNTs are observed in the NCs because, in the *in situ* chemical route, a stronger chemical grafting occurs at the TiO_2 /MWCNT interface.³⁰ The SAED pattern of the NCs shows good ring patterns with lattice points indicating crystallinity. The indexed ring designs closely match with the spacing of the various reflections of the anatase phase.

The optical properties of NCs powders were studied through UV–visible DRS spectra. Figure 5(a) includes UV–visible DRS spectra of bare TiO_2 NPs and the representative TiO_2 /MWCNTs NCs. All samples show the absorption edge between 382 and 400 nm due to the excitation of electrons from the valence band to the conduction band of the TiO_2 host material.²⁹ With the increase in MWCNTs content in TiO_2 , not

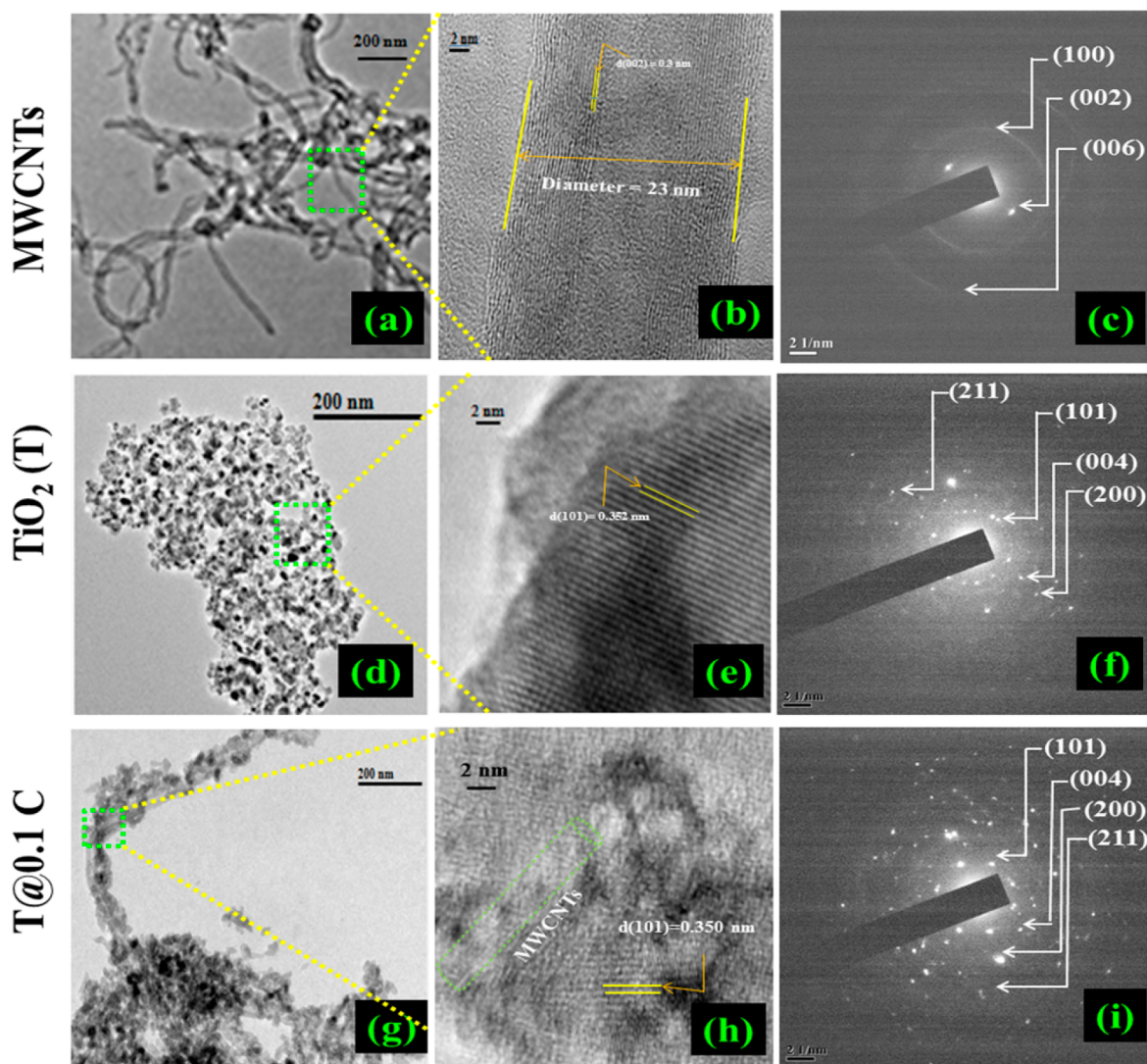


Figure 4. (a,d,g) TEM images, (b,e,h) HRTEM images, and (c,f,i) SAED patterns of MWCNTs, bare TiO_2 NPs, and T@0.1 C NCs.

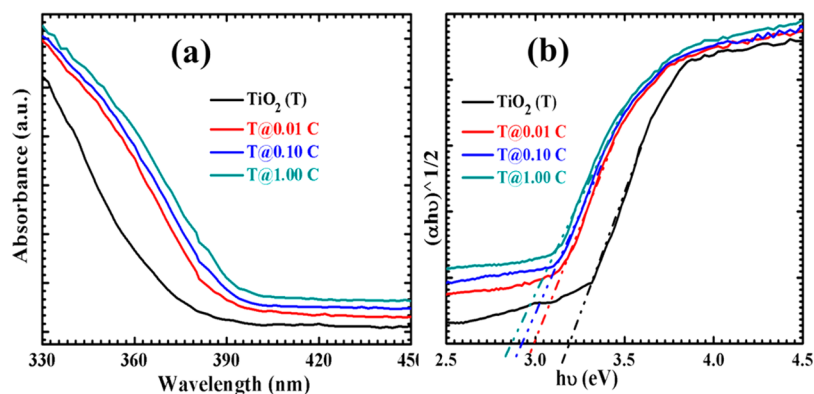


Figure 5. (a) UV-visible DRS spectra and (b) Kubelka–Munk function $(\alpha hv)^{1/2}$ as a function of photon energy ($h\nu$) of bare TiO_2 NPs and representative T@0.01 C, T@0.10 C, and T@1.00 C NCs.

only the absorption capability but also the red shifting of the absorption edge of NCs are also observed. This optical absorption behavior reveals the strong interaction between the TiO_2 and MWCNTs, which results in the enhancement of surface electric charge of the TiO_2 NPs by MWCNTs.

It is also beneficial for the ease of charge transfer between TiO_2 and MWCNTs and hence results in the enhancement of light absorption capability of TiO_2 in the visible region, which are excellent aspects for light-harvesting ability of the photoanode material.³¹ To know the impact of varying content of MWCNTs on the optical properties of TiO_2 , the optical

energy band gaps of all samples were determined. Optical energy band gaps of all the representative samples were calculated by using the Kubelka–Munk function $(\alpha h\nu)^{1/2}$ (where α is the absorption coefficient) as a function of photon energy ($h\nu$), which is shown in Figure 5(b). The optical energy band gap is recognized by plotting the intercept tangent to the x -axis in a graph, decreased from 3.2 to 2.85 eV with an increase in the content of MWCNTs in TiO₂ (Table 2) (Figure S7, SI). The calculated optical band gap is firm evidence for the visible-light absorption by NCs as compared to bare TiO₂ NPs.

Table 2. Optical Energy Band Gap, BET Surface Area, Amount of Dye Adsorbed (N719 and RuPc) on the Surface of the Bare TiO₂, and Representative NCs Samples

samples	optical band gap (eV)	surface area (m ² /g)	amount of dye adsorbed (mol/cm ²)	
			N719	RuPc
TiO ₂ (T)	3.20	90.27	3.00×10^{-5}	1.03×10^{-5}
T@0.1 C	2.90	109.85	3.23×10^{-5}	1.15×10^{-5}
T@1.0 C	2.85	60.42	2.47×10^{-5}	--

To study the electronic behavior as well as separation of photogenerated charge carrier trapping with the fate of excitons in the semiconductor materials, the photoluminescence (PL) studies of the various materials were investigated. The PL spectra of bare TiO₂ NPs and TiO₂/MWCNTs NCs in the wavelength range between 450 and 650 nm are presented in Figure 6.

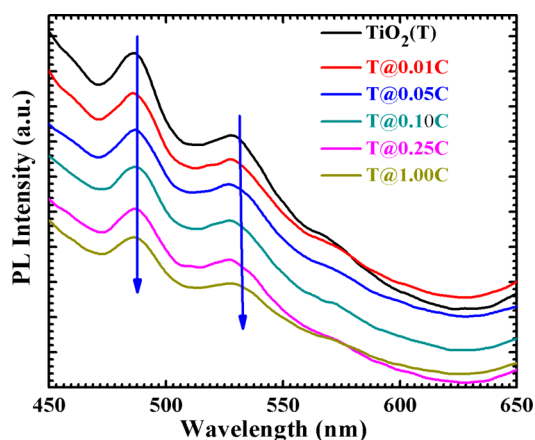


Figure 6. Photoluminescence emission spectra of bare TiO₂ NPs and TiO₂/MWCNTs NCs with varying content of MWCNTs.

The emission peaks appeared at 486 and 527 nm, corresponding to the band–band emission and metal–nonmetal charge transfer transitions by excitation wavelength at 365 nm (Figure S8, SI).³² With the increase in the content of MWCNTs, the PL intensity of the respective emission peaks decreases. The decreasing behavior of PL is attributed to reductions in the radiative recombination of photoinduced electrons trapped at the surface of TiO₂ with the content of MWCNTs, and hence NCs are best for the efficient charge separations. The detailed charge separation and energy level diagram of the photoelectrode are shown in the Supporting Information (Scheme S1, SI).

FT-IR spectra of MWCNTs, bare TiO₂ NPs, and representative NCs are shown in Figure 7. FT-IR spectrum

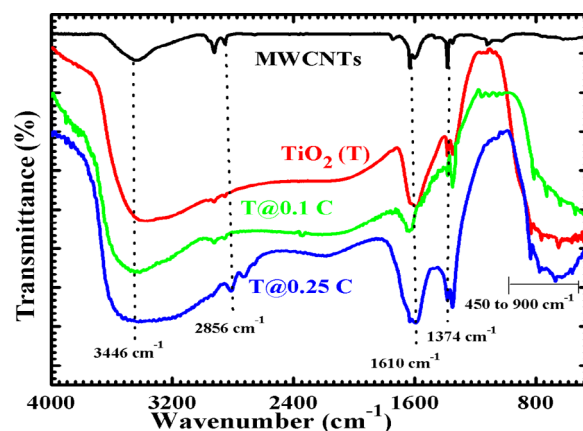


Figure 7. FT-IR spectra of MWCNTs, bare TiO₂ NPs, and representative T@0.1 C and T@0.25 C NCs.

of MWCNTs shows the peaks at 3440, 2925, 2845, 1740, 1632, 1383, and 1110 cm⁻¹ corresponding to the O–H stretching vibration, C–H stretching, C–OH stretching, C=O stretching, O–H deformation vibrations, and alkoxy C–O stretching vibrations, respectively.^{33,34}

FT-IR spectra of TiO₂ NPs or NCs show the broad absorption band from 3000 to 3400 cm⁻¹ assigned to the –OH stretching frequency vibration. The bands at the region 3000–3400 cm⁻¹ broaden, with the content of MWCNTs, reflecting the increase in surface hydroxylation of NCs. A band in the range of 2925–2856 cm⁻¹, analogous to the Ti–OH stretching vibration, is shifted to the lower frequency region at 2820–2730 cm⁻¹ in the TiO₂/MWCNTs NCs. The shifting is due to the –OH stretching frequency region of the Ti precursor overlapping with the other contributions like C=O, C–O, and O–C=O moieties of MWCNTs.²³ Similarly, other peaks at 1374 cm⁻¹ and 1590–1630 cm⁻¹ in the NCs are also shifted to the longer frequency region, which reveals the interaction between the carboxylate groups of MWCNTs with the Ti precursors.³⁰ The TiO₂ NPs or NCs samples show the broad peak in the range between 550 and 900 cm⁻¹, due to the various stretching vibrations such as Ti–O, O–Ti–O, Ti–O–C, and Ti–O–C=O.³⁵

The chemical composition and the chemical states on the surface of the elements are studied by using EDAX, which is illustrated in the Supporting Information (Figure S2, SI) and XPS analysis shown in Figure 8. Figure 8(a) shows the high-resolution core level spectrum of the Ti ion, and it consists of two peaks at 458.95 and 464.66 eV corresponding to Ti 2P_{3/2} and Ti 2P_{1/2} states, respectively. The difference in binding energy between the two peaks (5.69 eV) corresponds to the Ti⁴⁺ state in the octahedral environment of the anatase TiO₂.³⁶ Figure 8(b) shows the high-resolution core-level XPS spectrum of oxygen species. A major peak at 530.9 eV is due to the presence of lattice oxygen in the sample and is deconvoluted into two peaks at 531.4 and 532.6 eV and analogous to the carbonyl (–C=O) or carboxylic species from the TiO₂/MWCNTs NC.²⁹ The high-resolution C 1s core-level spectrum of the same sample is shown in Figure 8(c). A major peak at 284.8 eV is due to the sp²-hybridized carbon atoms, and it also deconvoluted into four peaks at 284.85, 285.26, 285.57, and 289.28 eV corresponding to the sp²-bonded carbon atoms of C=C, C–O, C=O, and ester groups (O–C=O), respectively. The existence of all these groups is beneficial for making the chemical bond formation between the TiO₂ lattice and

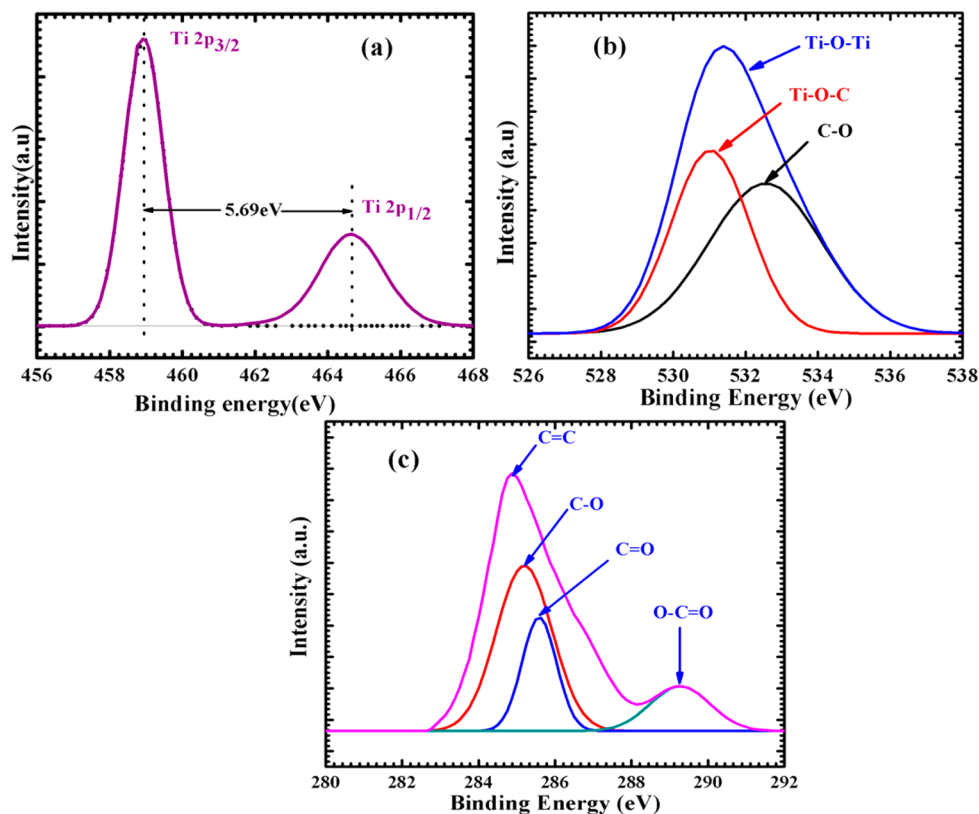


Figure 8. High-resolution XPS spectra of (a) Ti 2p, (b) C 1s, and (c) O 1s core-level spectra of T@0.1 C NCs powder.

MWCNTs, and the absence of the other peak at 281 eV indicates that elemental carbon is not doped in the TiO₂ lattice.³⁷

Brunauer–Emmett–Teller (BET) analysis gives the specific surface area of the materials. Figure 9 shows the nitrogen (N₂)

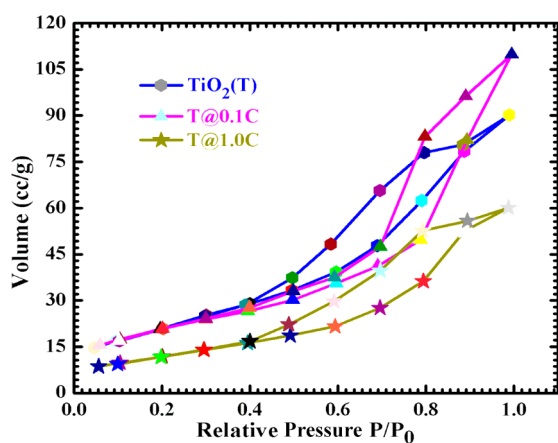


Figure 9. N₂ adsorption isotherms of bare TiO₂ NPs and representative T@0.1 C and T@1.0 C NCs.

adsorption–desorption isotherms of bare TiO₂ NPs, representative T@0.1 C, and T@1.0 C NCs. The separation between the N₂ adsorption–desorption curves indicates that samples exhibit type IV isotherms.³⁸ T@0.1 C NCs as well as bare TiO₂ show that the N₂ adsorption rises abruptly due to the capillary condensation of N₂ and leading to the formation of type H1 hysteresis loops. It also signifies the particles with spherical pore geometry and a high degree of pore size

uniformity, while in the case of T@1.0 C NCs, the decrease in N₂ adsorption is observed due to the reduction in surface area and also improper anchoring of TiO₂ NPs on the surface of MWCNTs.³⁹ The BET parameters of the samples are summarized in Table 2.

The specific surface area of bare TiO₂ is found to be 90.27 m²/g, which is intermediate between the surface area of T@0.1 C (109.85 m²/g) and T@1.0 C (60.42 m²/g) samples. Overall, it reveals that the least addition of MWCNTs in the NCs increases the surface area to the TiO₂ matrix due to the proper anchoring of TiO₂ on the surface of the MWCNTs.⁴⁰ In the design of the photoelectrode, the N719 dye is directly anchored on the surface of the NCs thin films through carboxylic groups of the N719 dye.⁴¹ However, due to the absence of carboxylic groups, RuPc is not directly anchored to the surface of the NCs thin films. Therefore, isonicotinic acid (INA) is used as a bridging ligand to connect RuPc with the surface of the NCs thin films, and hence the overall connectivity of RuPc with NCs through INA is similar to that of N719 dye. The bridging role of INA is confirmed by measuring the absorption spectra of TiO₂/MWCNTs with and without INA, which is shown in the Supporting Information (Figure S9, SI). In comparison, the optical absorption of the TiO₂/MWCNTs/INA/RuPc photoelectrode is higher than that without INA (TiO₂/MWCNTs/RuPc). The optical behavior powerfully reveals that INA binds steadily to both dye and host materials, viz., the dye molecule through the pyridine ring and TiO₂/MWCNTs through carboxylic acid moieties (Scheme 1).

After anchoring with dyes, the photoanodes further characterized by using UV–visible absorption spectroscopy. The UV–visible absorption spectrum of the TiO₂-MWCNTs/N719 photoelectrode shows two characteristics absorption bands of N719 in the range 310–600 nm (Figure 10). The first

Scheme 1. Schematic Representation of the Sandwich Structure of DSSCs Having either Dye (a) N719 or (b) RuPc Anchored Nanocrystalline TiO₂/MWCNT Composites as a Working Electrode and Pt/ITO as the Counter Electrode along with the Redox Mediator

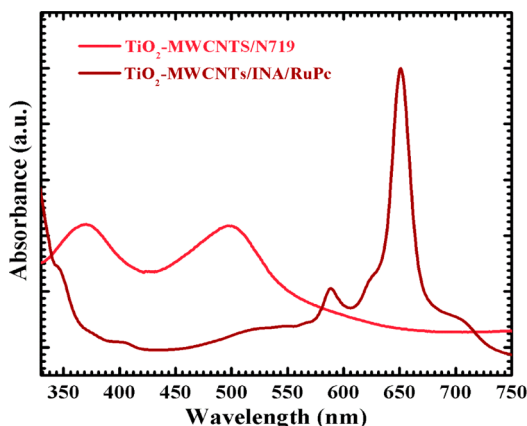
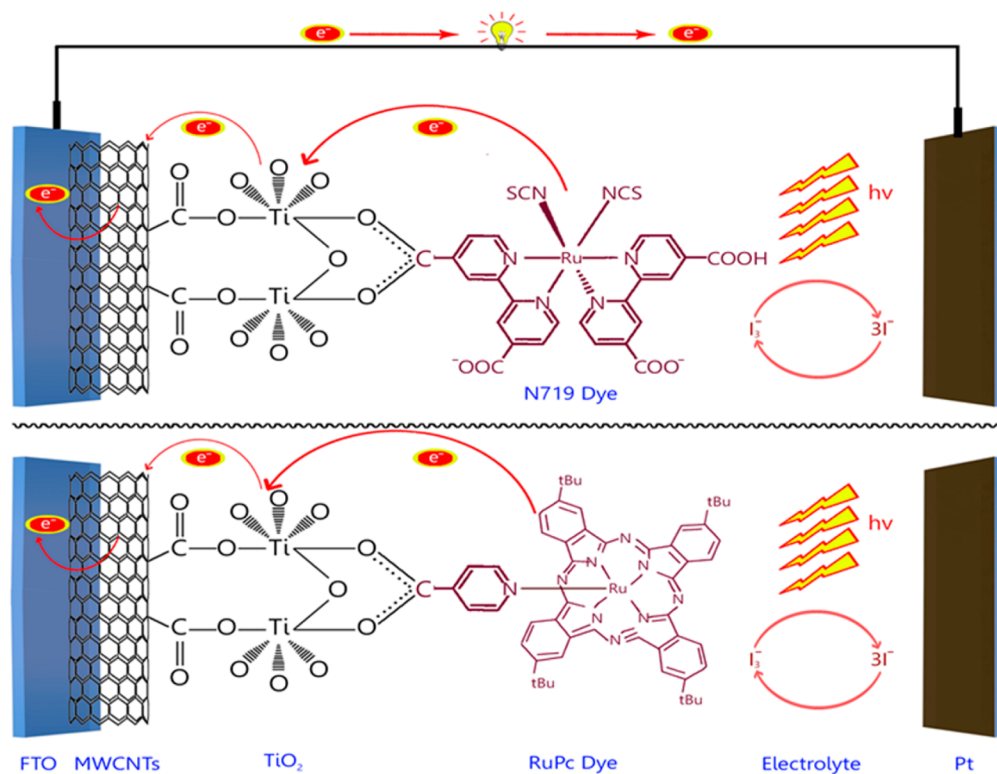


Figure 10. UV–visible absorption spectra of TiO₂/MWCNTs/N719 and TiO₂/MWCNTs/INA/RuPc based photoanodes.

band appeared at 370 nm due to the π – π^* transition of the aromatic rings, and the second band is at 502 nm due to the internal charge transfer transition.⁴² Similarly, the TiO₂/MWCNTs/INA/RuPc photoanode shows the characteristic Q-band of RuPc at 650 nm, where the maximum solar photons occur.⁴³ In addition to the Q-band, it also absorbs the light to a small extent at the various regions of the electromagnetic spectrum. The bands in UV–visible patterns are characteristic absorptions of individual ingredients present in the photoelectrodes.

After that, the amount of N719 and RuPc dyes was loaded on the surface of the NCs thin films measured by desorbing a 1.0 cm² area of the dye adsorbed thin films into the 5 mL aqueous 1 mM KOH solution. It is evident from Figure 11(a) that the

absorption spectra of N719 dye were detached from the TiO₂ NPs and representative NCs thin films. It shows the two distinct absorption maxima at 370 and 500 nm, but the actual N719 dye shows maximum absorption peaks at 380 and 518 nm. The shifting to the 370 and 500 nm is due to the anchoring of the N719 dye molecules on the surface of the NCs thin films.⁴² RuPc shows the absorption maxima at 650 nm [Figure 11(b)] due to the characteristic Q-band. The quantification of dye adsorbed on the thin-film surface is calculated from Figure 11(a and b) and illustrated in Table 2. The observed result shows the T@0.1 C NCs photoelectrode having the maximum dye adsorption capability as compared to the bare TiO₂ NPs and other NCs thin films. It is fascinating that the dye loading capacity of T@0.1 C NCs is higher as compared to the bare TiO₂ NPs and other NCs based photoelectrodes. Hence, the high loading of dye offers the better harvesting of photons in the visible range of dyes and will increase the photocurrent density (J_{sc}) of the devices.

The sensitized photoanodes were used for sandwich-type DSSCs (Scheme S1, S1) and further tested for photovoltaic performance using a solar simulator under standard AM 1.5 one sun illumination (100 mW/cm²) with an active area of 0.25 cm². In addition to the assessment of the sensitizer's impact, the effect of MWCNTs on the photovoltaic properties of the TiO₂ host lattice with the N719-based DSSC device showed different solar cell parameters. Figure 12(a,b) shows the current density–voltage characteristic curves of the samples with N719 and RuPc dyes, respectively.

The different photovoltaic parameters such as photocurrent density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and light to electrical conversion efficiency (η) of the DSSCs are represented in Table 3.

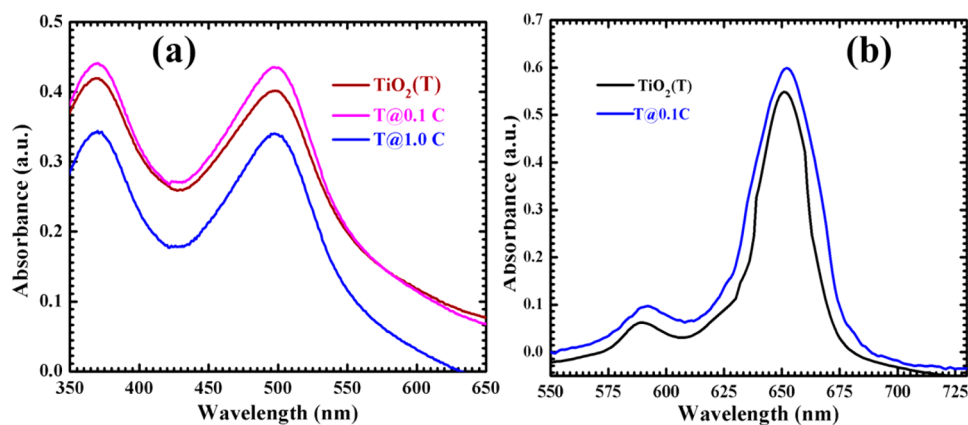


Figure 11. UV-vis absorption spectra of solutions containing (a) N719 and (b) RuPc dyes detached from bare TiO₂ and representative NCs thin films (all with 1.0 cm² area) in 5 mL of aqueous solution of 1 mM KOH.

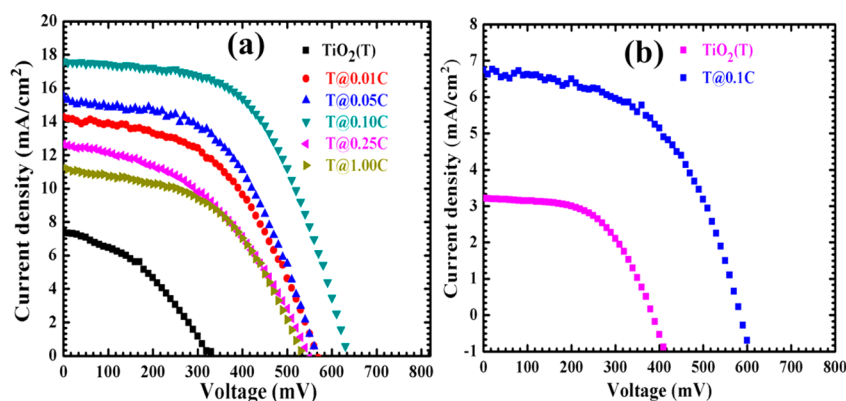


Figure 12. Photocurrent density vs voltage curves of (a) bare TiO₂ and TiO₂/MWCNTs NCs with varying composition of MWCNTs for N719 and (b) bare TiO₂ and T@0.1 C NCs for RuPc-based DSSC devices.

Table 3. Photovoltaic Parameters of Bare TiO₂ NPs and TiO₂/MWCNTs NCs with N719- and RuPc-Based DSSC Devices

samples	MWCNT content (wt %)	solar cell parameters			
		J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	η (%)
For N719 Dye					
TiO ₂ (T)	0.00	07.37	0.330	43.77	1.04
T@0.01C	0.01	14.27	0.560	49.48	3.95
T@0.05 C	0.05	15.50	0.560	51.72	4.49
T@0.1 C	0.10	17.60	0.630	56.08	6.21
T@0.25 C	0.25	12.64	0.540	44.61	3.04
T@1.0 C	1.00	11.24	0.530	50.21	2.99
For RuPc Dye					
Bare TiO ₂	0.00	0.46	0.300	57.49	0.07
T@0.1 C	0.10	6.73	0.580	53.24	2.07

In the case of FTO/TiO₂-MWCNTs/N719 DSSCs, the overall highest power conversion efficiency of 6.21% is noted for T@0.1 C NC-based DSSCs. This highest efficiency of T@0.1 C NC-based DSSCs is also reflected through its highest values of J_{sc} (17.60 mA/cm²), V_{oc} (0.630 V), and FF (56.08%). However, the J_{sc} value of other NC-based DSSCs varied from 11.24 to 15.50 mA/cm² (Figure 13(b)). Specifically, the J_{sc} value is increased up to T@0.1 C NC-based DSSCs, and after that, it decreased to 11.24 mA/cm² for T@1.0 C NC-based DSSCs, which is shown in Table 3. It is also interesting that the

J_{sc} value of NC-based DSSCs is higher than that of bare TiO₂-based DSSCs. This change in J_{sc} value of NCs or bare TiO₂-based DSSCs is collinear with the change in surface area of NCs as well as dye loading capacity of NC-based photoelectrodes (Table 2). In addition, the J_{sc} value of TiO₂/MWCNTs/N719 DSSCs is higher than that of TiO₂/MWCNTs/RuPc DSSCs; this is attributed to the reasons such as connectivity between the host material and dye and coverage of optical region. In the case of N719-based DSSCs, the direct connectivity between N719 and TiO₂/MWCNTs is observed, while in RuPc-based DSSCs the INA acts as a bridging ligand between TiO₂/MWCNTs and dye. Though absorption is higher for RuPc dye, the coverage region is small. Hence, the synergetic effect of these factors is responsible for an improved charge-carrier transport resulting in an increase in J_{sc} values of TiO₂/MWCNTs/N719-based DSSCs.⁴⁴

A plot of V_{oc} as a function of MWCNTs composition in TiO₂ is shown in Figure 13(c). It revealed that no significant change is observed for V_{oc} value in NC-based DSSCs except T@0.1 C NC-based DSSCs. The V_{oc} value of NC-based DSSCs is seen around 0.550 V, which is still lower than that for bare TiO₂-based DSSCs. The lower photovoltage is attributed to the nearly same absorption edge of the NC photoelectrodes, while in the case of FF value the change is similar to that of J_{sc} as well as the efficiency of DSSCs. Up to T@0.1 C NC-based DSSCs, the FF value increased to 56% from 43%, and after that, it decreased for higher content of MWCNTs in the TiO₂ host lattice, which is shown in Figure 13(d). Moreover, the

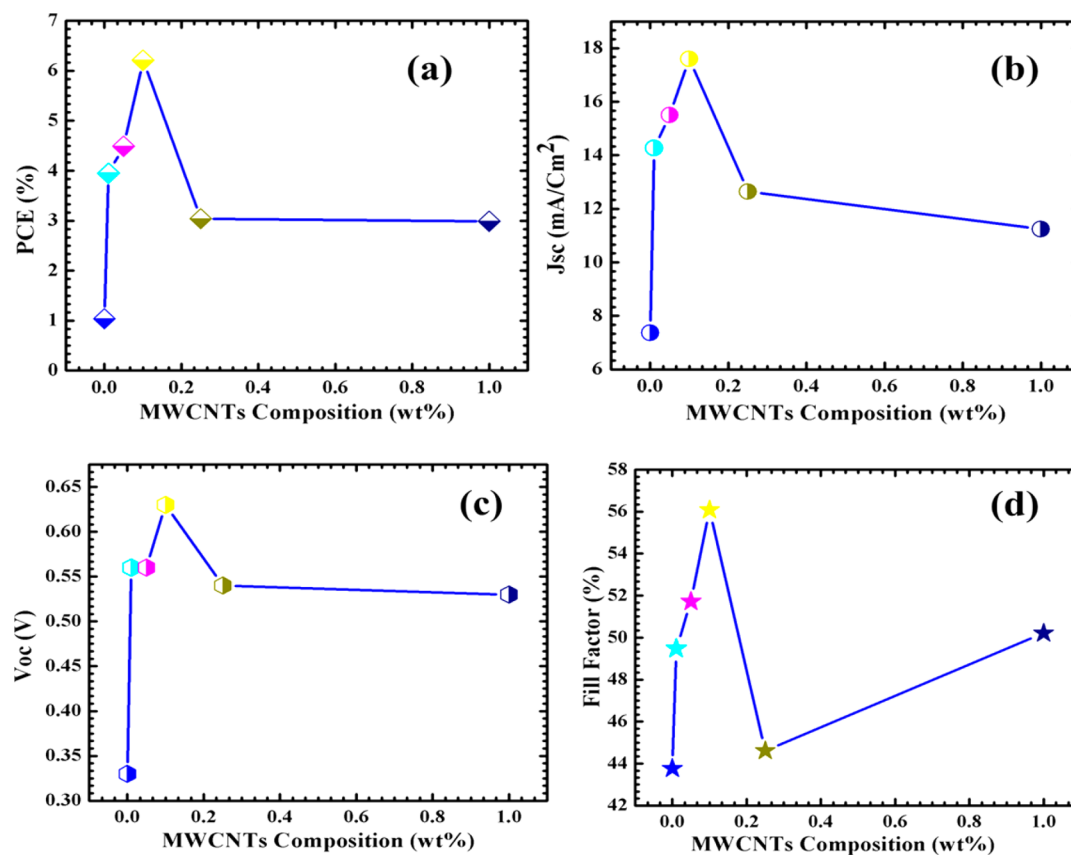


Figure 13. Plot of MWCNTs content (wt %) in the TiO₂ host lattice as a function of (a) η , (b) J_{sc} , (c) V_{oc} , and (d) FF. [Conditions: substrate: FTO, dye: 0.3 mM N719 in 1:1 ratio of tertbutyl alcohol and acetonitrile, electrolyte: 1.0 M LiI + 0.06 M I₂ in propylene carbonate, area: 0.25 cm², counter: Pt-deposited ITO, light source: 300 W xenon lamp with AM 1.5G filter.]

efficiency of all NCs-based DSSCs is in the range of 2.99–6.21%, which is three to six times more than that of bare TiO₂-based DSSCs (1.04%) [Figure 12(a)]. From the photovoltaic analysis of TiO₂/MWCNTs NCs with N719 dye sensitization, it is concluded that the highest solar to electrical conversion efficiency is observed for T@0.1 C NCs-based DSSCs, and hence, for further photovoltaic studies with RuPc dye, only the T@0.1 C NCs-based photoelectrode is used. In the case of RuPc, T@0.1 C NC-based DSSCs result in a power conversion efficiency of 2.07%. The other photovoltaic parameters of T@0.1 C NC-based DSSCs are J_{sc} (6.73 mA/cm²), V_{oc} (0.580 V), and FF (53.24%). Overall, the power conversion efficiency of the TiO₂-based DSSC device is low as compared to the TiO₂/MWCNTs NC-based DSSC device. In DSSCs, the excited electrons (LUMO) from the dye are injected into the conduction band (LUMO) of TiO₂ and finally transferred into the counter electrode through two ways, namely, electric field driven charge transport⁴⁵ and a trap-limited diffusion process.⁴⁶ However, in bare TiO₂ the electron transport is negligible because the diffusion of electrons through the TiO₂ network undergoes different interfaces, and these interfaces act as electron trap centers, and hence there is a possible electron–hole pair recombination.⁴⁷ However, in TiO₂/MWCNTs NCs-based DSSC device the MWCNTs acts as a carrier transporter with proper channels, and hence it avoids the possibility of recombination; that is, it minimizes the charge transport resistance of the device. Once the excited electron from the dye is injected into the semiconductor, it has an efficient pathway to reach the counter electrode through

MWCNTs, and hence it greatly enhances the photoresponse of the cell.⁴⁸

In the end, with varying sensitizers, the photovoltaic performance of T@0.1 C NCs-based DSSCs is significantly higher. The power conversion efficiency of T@0.1 C NCs/N719 DSSCs is almost three times more than that of RuPc-based DSSCs, and hence the overall efficiency reaches 6.21% from either 1.04% of bare TiO₂ with N719 or 0.07% of bare TiO₂ with RuPc. It is interesting that although there is a resemblance in the connection of dyes with the surfaces of TiO₂-MWCNTs the conversion efficiency of DSSCs with different dyes is different due to their optical absorption coverage. Overall, the energy conversion efficiency of T@0.1 C NCs/N719 DSSCs is higher than others (T@0.1 C NCs/RuPc, TiO₂/N719, and TiO₂/RuPc DSSCs). Along with the surface area of the host material, the higher efficiency is correlated to the well coverage of the electromagnetic spectrum by N719-based DSSCs, resulting in more absorption of light with the formation of efficient charge carriers, which is responsible for the significant enhancement of the conversion efficiency. The detailed absorption edge and absorption strength of the two different sensitizer-based DSSCs is discussed in the incident photon-to-charge carrier conversion efficiency (IPCE) measurement.

The photovoltaic performances of the N719 and RuPc-based DSSC devices are confirmed by using IPCE at different incident wavelengths and determined by using the following relation

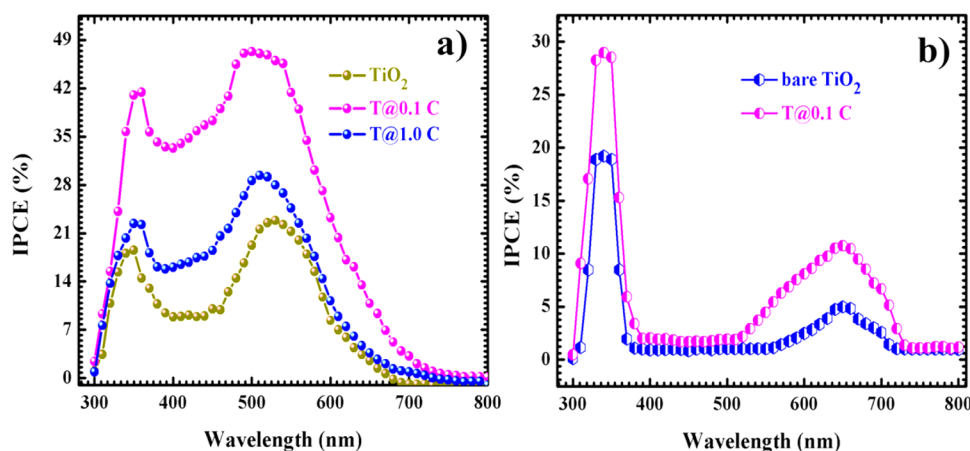


Figure 14. IPCE spectra of bare TiO₂ NPs and representative NCs for (a) N719 and (b) RuPc-based DSSCs.

$$\text{IPCE (\%)} = \frac{\left[1240 \times J_{\text{sc}} \left(\frac{\text{A}}{\text{cm}^2} \right) \right]}{\left[\lambda \text{ (nm)} \times I_{\text{inc}} \left(\frac{\text{W}}{\text{cm}^2} \right) \right]} \times 100$$

where J_{sc} is the short-circuit current density; λ is the wavelength of the incident light; and I_{inc} is the power of the incident light.⁴⁹ Figure 14(a, b) shows the IPCE spectra for the N719- and RuPc-based DSSCs, respectively. In the case of an N719 dye, the photocurrents for all TiO₂-MWCNT NC-based DSSCs are generated in the range from 300 to 650 nm. The two distinct regions (viz., 300–400 nm and 475–650 nm) are observed for current generations.

The former region is found due to the characteristic absorption of TiO₂ as well as the small extent of N719 dye, while the latter is due to the high absorption of the N719 dye.²³ The maximum IPCE value of TiO₂/MWCNTs NC-based DSSCs reached 47% for T@0.1 C NCs/N719-based DSSCs as compared to others, which is also in good agreement with the observed maximum J_{sc} of the TiO₂/MWCNT NCs-based DSSCs. In comparison to bare TiO₂-based DSSCs, the IPCE value for T@0.1 C NCs-based DSSCs is 2.5 times higher. Similar to I - V characterization, the loading of N719 dye and MWCNTs content in the TiO₂ host lattice enhances the optical properties of the TiO₂ host lattice, and it is better for the charge separation as well as the efficiency of the cells.²⁸ In the end, IPCE response of T@0.1C NC with RuPc dye through INA was tested under the same operating conditions. It shows the two distinct absorption maxima, viz., between 300 to 400 nm and 600 to 700 nm, for the conversion of solar to electrical current. The first region is dominated due to the absorption of TiO₂, and the second wide region is analogous to RuPc only, with minimum absorption to that of the N719 dye. Overall, the IPCE value of TiO₂/MWCNTs NCs/N719 based DSSCs is almost three times that of the TiO₂/MWCNTs NCs/INA/RuPc-based DSSCs. Because through carboxylic functional groups N719 is covalently connected to the surface of the TiO₂/MWCNTs NCs, the connectivity of the different moieties results in the high absorption capacity of the cells. Due to the absence of carboxylic functional moieties, RuPc was anchored on host materials through INA, but it may also build up the resistivity of the cells and hence decrease the overall conversion efficiency of the RuPc-based DSSCs. The lower power conversion efficiency confirms that, along with MWCNTs content, the proper connectivity between the dye

and MWCNTs plays a dominant role in capturing as much incident light as possible by its absorption strength with host semiconducting material and overlaps that possible absorption with the solar spectrum.

CONCLUSIONS

Thin films of TiO₂/MWCNT NCs were successfully deposited on FTO-glass substrate using a binder-free doctor blade technique. The anchoring of TiO₂ NPs to the surfaces of MWCNTs was confirmed by using HRTEM, FT-IR, Raman, and XPS analysis. With varying MWCNTs content in NCs, the structural parameters of the TiO₂ host lattice were varied, which was also confirmed by Rietveld refinement studies (goodness of fit = ~1.5). The optical absorption edge of TiO₂ extended toward the red region of the electromagnetic spectrum with MWCNTs, and the optical energy band gap of samples turned from 3.2 to 2.85 eV. The TiO₂/MWCNTs NCs are anchored with two different Ru(II)-based dyes, viz., N719 and RuPc, and these electrodes were used as photoanodes for efficient DSSCs. The different absorption and anchoring nature of sensitizers directly affected the solar energy power conversion efficiency of the devices. Among all devices, T@0.1C NCs with N719-based devices showed the highest J_{sc} , V_{oc} , FF, and η (6.21%) as that of either other CNTs-based devices or the RuPc-based DSSCs device ($\eta = 2.07\%$). The same materials were utilized toward the fabrication of solid-state DSSCs (using either p-type inorganic or p-type organic semiconductors as HTMs), and works are in progress in our lab.

EXPERIMENTAL SECTION

The commercial pristine MWCNTs were functionalized with the acid treatment method,⁵⁰ and bare TiO₂ NPs were synthesized by an earlier reported sol-gel method with slight modifications.⁵¹ The phthalocyanine (Pc) based Ru(II) complex (RuPc) was prepared by using a literature method with some modifications.⁵² The detailed experimental conditions of all these materials have been provided in the Supporting Information.

Synthesis of TiO₂/MWCNTs Nanocomposites (NCs). An *in situ* sol-gel method was used for synthesizing TiO₂/MWCNT NCs with varying content of MWCNTs. The functionalized MWCNTs were dispersed in deionized water (DW) using an ultrasonicator bath, and these MWCNTs were added directly during the synthesis of the TiO₂ NPs route after

hydroxylation of titanium precursors. The blackish colored precipitate formed and was subsequently washed, dried, and annealed at 753 K for 2 h. The different contents of MWCNTs such as 0.01, 0.05, 0.1, 0.25, and 1.0 wt % were added to the titanium precursor, and then these samples are designated as T@0.01 C, T@0.05 C, T@0.1 C, T@0.25 C, and T@1.0 C, respectively.

Fabrication of DSSCs with TiO₂/MWCNTs Photoanodes. Binder-free NCs were deposited on FTO glass electrode using the doctor-blade technique. Primarily, FTO glass substrates were washed thoroughly with water (with detergent), acetone, and finally in ethanol using an ultrasonic bath. The cleaned glass substrates were annealed at 373 K for 30 min. The NC powders were ultrasonically dispersed in both *N,N*-dimethylformamide (DMF) and acetonitrile (ACN) for 1 h and 30 min, respectively, and the upper organic layer was decanted. The remaining portion was stirred continuously to form slurry. This slurry was deposited on a cleaned FTO glass substrate using the doctor-blade method, and these films were sintered at 723 K for 2 h. The deposited thin films were sensitized using, namely, N719 and RuPc dyes separately. In sensitization protocol, thin films were immersed in 0.3 mM N719 dye solution (1:1 mixture of *tert*-butyl alcohol and ACN) for 18 h (room temp). The unbound dye was removed from the film after rinsing twice in a combination of *tert*-butyl alcohol and acetonitrile. The N719 dye-anchored photoelectrode was sandwiched between the platinum counter electrode (Pt/ITO) using 60 μm thick sealing Surlyn sheet. Finally, the electrolyte (1.0 M LiI + 0.06 M I₂ in propylene carbonate) was impregnated and sealed (Scheme 1). The photovoltaic performance of the devices (with an active area of 0.25 cm²) was measured by the current–voltage (*IV*) and IPCE spectra. Similarly, the photovoltaic performance of the sandwich-type DSSCs with TiO₂/MWCNTs (T@0.1 C) photoelectrode, sensitized with RuPc dye, was also measured.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01316.

The thermal stability (TGA) and structural parameters of as-synthesized materials, position coordinates and atom occupancies of TiO₂, XRD refined patterns of T@0.01 C, T@0.05 C, T@0.25 C, and T@1.00 C, MWCNTs composition (wt %) as a function of optical energy band gap, and photoluminescence excitation spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: sdddelekar7@gmail.com (Sagar Delekar).

*E-mail: dpanda@g.clemson.edu (Dr. Dillip K. Panda). Tel.: +91-231-2609100. Fax: +91-231-2692333.

ORCID

Sagar D. Delekar: 0000-0002-4510-305X

Naresh S. Dalal: 0000-0002-9996-6918

Author Contributions

#S.D.D. and A.G.D. contributed equally

Author Contributions

The final version of the manuscript was approved by all authors.

Notes

The authors declare no competing financial interest.

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