Dual Morphologies of Titanium Dioxide for Dye Sensitized Solar Cells

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ABSTRACT

Anatase TiO₂ displaying dual morphologies were synthesized with a simple chemical route via a single step. A strong correlation between the dye sensitized solar cell (DSSC) device performance and the obtained dual morphologies are highlighted using relevant evidences from UV-vis and diffuse reflectance spectroscopy (DRS), Raman analysis, field emission scanning electron microscope, high resolution transmission electron microscope, current-voltage characteristics and impedance analysis. Structural investigation revealed that the interested medium in this work employed for the synthesis of TiO₂ produced different types of dual morphologies such as nanospheres with nanoparticles (NSNP), microsphere decorated with nanoparticles (μ SNP) and nanoparticles with stone like features (NPS). UV-vis and DRS results indicated the ability of the materials to assist with diffused reflectance and optical absorption of the screen printed photoanodes. In addition, an investigation of Raman vibrational characteristics was carried out in detail using synchronous and asynchronous 2D correlation analysis. The high intense Eg anatase mode of Raman spectrum was simulated using a phonon confinement model and its normalised spectra are compared with an experimental data. The resultant performances in the DSSCs were not indicative by the material properties; so, the charge transfer resistance (R_{ct}) and recombination properties of the photoanode were investigated. These results showed that the Nyquist plot of NSNP possesses the smallest diameter, which reveals that the device based on NSNP offers the lowest R_{ct} value that accounts for the higher conversion efficiencies when compared with the DSSC device based on photoanodes μ SNP and NSP. It can be concluded that the improved power conversion efficiency shown by photoanode fabricated using NSNP has the dual role of optimum surface area for dye loading and light scattering centres. These properties, when optimized along with the offered pathway for electrolyte diffusion to the dye degeneration with less R_{ct} , could lead to better photoelectric conversion efficiency.

Key words:

Composites, Screen Printing, 2D correlation, Phonon confinement, Dye Sensitized Solar Cell

1 Introduction

Grätzel and co-workers invented the dye sensitized solar cell (DSSC) with titanium dioxide (TiO₂) nanostructure-based photoanodes. A conversion efficiency of 7.1% was reported with TiO₂ colloidal solution coated fluorine-doped tin oxide (FTO) substrate with ruthenium (Ru) sensitizer [1]. This seminal work created a significant interest in the research community because of the potential for low-cost solar cell production, an easy manufacturing process, and promising power conversion efficiency [2], [3], [4]. Tremendous efforts have been invested by various research groups to improve the photon to electron conversion efficiency of DSSC [5], [6], [7], [8]. Photovoltaic performance of the DSSC system depends on several parameters including the absorption range of the sensitizer, molar absorption coefficient, high performance electrolyte for the regeneration of dye, sheet resistance of the conducting transparent substrates and photochemically stable semiconductor materials [9], [10], [11], [12].

Much current research has been devoted to improving in the efficiency of DSSC by replacing standard Ru dyes with organic dyes, and developing photoanodes with various metal oxide semiconductors such as zinc oxide (ZnO), TiO₂ and tin oxide (SnO₂) [13], [14], [15], [16], [17]. Among these, titanium dioxide is one the most investigated photo anode material for DSSCs, because of its high chemical and thermal stability, low cost, high refractive index and favourable conduction band edges for efficient electron injection to many sensitizers [12], [18], [19]. The photovoltaic performance of the DSSC's strongly depends on the physical and structural properties of TiO₂, including crystal size, morphology, phase composition, porosity, thickness of TiO₂ layer, specific surface area in order to achieve strong light scattering capacity, dye loading ability, electron hole pair separation efficiency, electron transport and diffusion of electrolyte [20], [21], [22], [23].

The first DSSC device was assembled with TiO₂ nanoparticles, which have the advantage of large surface area for efficient dye loading, but are suboptimal because of random electron path ways and dead ends that hamper electron transport [24]. The development of one dimensional (1-D) nanostructures such as nanorods [25] nanowires [26] and nanotubes [27] have been proven to provide superior directional pathways for the electrons to reach the conductive substrates as compared to nanoparticles. These 1-D nanostructures reduce the number of dead ends for electron transport [28]. 1-D nanostructures, however have some drawbacks including reduced dye loading [29], [30]. Thus, fully three dimensional (3-D) structures with different granules have been reported in an attempt to overcome these limitations in one dimensional and zero dimensional structures of TiO₂ based DSSC [31].

Recent works have focused on developing dual nanostructures that combine two different morphologies like nanospheres and nanoparticles, nanorods with nanoparticles [32], [33]. Dual morphologies have shown promising synergism over the individual morphology based photoanodes and better performance with reference to bilayer working electrodes of compact layers over scattering layers [34], [35]. The compact layer formed by small sizes of nanoparticles has a higher surface area which provides a greater number of sensitizer molecules anchoring locations resulting in greater absorption and potential for photoelectron conversion [36]. Even though scattering layers offer better light scattering abilities, they can also result in decreasing surface area, which is a cause of interfacial charge transfer resistance [37].

The potential benefits of the use of dual morphology nanomaterials are that the optimum surface area can be tuned for efficient dye loading while the nanomaterials can also be tuned to provide optimal light scattering. In addition, the dual role of dual morphological nanomaterials support for better electron mobility and diffusion of electrolyte can improve performance of DSSC [38]. Dual morphology nanomaterials have been represented in some previously reported articles as nanocomposites [32], [39]. Liang et al. employed hydrothermal method to prepare anatase TiO₂ microspheres with interconnected nanoparticles, which offered a photovoltaic conversion efficiency of 7.13% at an optimum thickness of 14.5 μm [40]. Ilayaraja et al. synthesized TiO₂ microspheres and higher conversion efficiency of 8.94% was achieved using dual morphology composite based photoanode by mixing 80 weight percentage of TiO₂ synthesized microsphere and 20 weight percentage of P25 powder. This 80/20 mixed composite structure provides a higher surface area for better dye loading, and the interconnected sphere and particle nature helps in efficient electron transport, which results in better light harvesting capacity [32].

To build on that work, in this study, TiO₂ dual morphologies including nanospheres with nanoparticles, microsphere decorated with nanoparticles and nanoparticles with stone like structures were prepared by a simple and one step reflux method. To the best of our knowledge, the projected synthesis mechanism is easy and less time-consuming when compared to already reported methodologies for the preparation of nanocomposites [40]. This work makes a significant contribution to the composite structure based TiO₂ photoanode performance towards the incident photon to electron conversion efficiency.

2. Experimental section

2.1. Materials and methods

The following chemicals were used to synthesize and fabricate TiO₂ composites without any further purification. Titanium (IV) butoxide (TBT, 97% purity), ethanol AR (99.9%), acetic acid (AcOH, 99–100%), ammonia solution (25%, Merck), double distilled water, titanium tetrachloride (99.5%, Loba chemie), N719 – dye (Sigma), fluorine-doped tin oxide coated glass plate (F-doped SnO₂:13 Ω/sq, sigma), chloroplatinic acid solution 8 wt% in H₂O (Sigma Aldrich), 4-tert-butylpyridine, iodide (I₂), lithium iodide (LiI).

2.2. Synthesis of TiO₂ composites

150 ml of ethanol was taken in a round bottomed flask. 0.12 M of titanium butoxide was dissolved under continuous stirring and refluxed at 80 °C. 90 ml of water was added into the above solution. The experimental condition was maintained for 1 h and marked as NSNP. The same procedure was followed as for the sample, with an addition of required amount of acetic acid (pH-4.5) ammonia (pH-9), respectively named as sample μPNP and sample NPS. The precipitate was filtered and washed with ethanol and dried at 80 °C. The obtained powders were calcinated at 470 °C for 1 h using a muffle furnace.

2.3. Preparation of photoanodes

A screen printable paste was prepared by mixing the annealed TiO₂ powders as described in Section 2.2 with glycerol using an agate mortar and pestle. Prior to the deposition, FTO glass substrate was washed with Triton-X 100, followed by distilled water and acetone using an ultrasonic bath. The conductive side of the FTO substrate was pre-

treated with 90 mM TiCl_4 solution at 70 °C for 30 min. Pre-treatment was followed by sintering at 450 °C for 30 min in an air atmosphere. The TiO_2 paste was coated on the TiCl_4 treated FTO substrate ($0.5\text{ cm} \times 0.5\text{ cm}$) using the screen printing method (AT-45PA). Subsequently, the coated films were annealed at 450 °C for 30 min using a muffle furnace. Post- TiCl_4 treatment was performed by following the same procedure followed for the pre TiCl_4 treatment. Sensitization was performed by soaking the photoanodes in an anhydrous ethanol solution containing 0.5 mM N719 dye for sixteen hours in the dark at ambient temperature. Pt counter electrode was prepared by 1 mM of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ solution in 2-propanol over the conductive substrate of FTO by drop casting method, followed by annealing at 450 °C for 30 min. DSSCs were assembled by clipping counter electrodes over the photoanodes. The space between the sandwiched electrodes was filled with a based liquid electrolyte containing 0.3 M 4-tert-butylpyridine, 0.5 M iodide, 0.05 M lithium iodide in acetonitrile.

2.4. Characterization

In order to identify the phase and crystal size of prepared powder samples, crystallographic characterization was performed using Rigaku ultima IV X-ray diffractometer with $\text{Cu-K}\alpha$ radiation. Morphology and nanostructural details of the synthesized materials were analysed using field emission scanning electron microscopy (FESEM, TESCAN MIRA 3) and high resolution transmission electron microscopy (HRTEM, FEI-TECNAI T20 G2). A UV-vis-NIR spectrometer was employed to investigate the light scattering abilities and dye loading capacity of photoanodes. (JASCO V770 Japan). Raman spectra were recorded using micro Raman spectrometer with excitation wavelength of 633 nm using a He-Ne laser. The shift of Raman bands with respect to particle sizes was analysed using shidge 2D software developed by Noda [41]. The electron transfer and recombination properties of the fabricated DSSCs were investigated using electrochemical impedance spectra measurements with a CHI600 electrochemical analyzer. Photocurrent-voltage measurements of DSSCs were carried out using a Keithley 2400 source meter under one sun illumination (AM 1.5). I-V and electrochemical measurements were performed in an open cell configuration.

3. Results and Discussion

3.1. Synthesis Mechanism

The dual morphological nanostructures were obtained using a predefined general synthesis mechanism which is detailed as follows. The precursor of Ti source undergoes two important steps in the adopted synthesis mechanism of this present work. First, the process of hydrolysis takes place with the aid of a solvent and a hydrolysis agent of alcohol water system. During hydrolysis, the Ti precursor forms a Ti-OH network by replacing its butoxide groups. The second process of condensation occurred between Ti-OH-OH-Ti networks, as they form a non hydrolytic network of Ti-O-Ti from the hydrolytic occurred during the previous process [42], [43]. The precipitation of TiO_2 occurring at the end of the whole process is represented in the schematic diagram of Fig. 1.

There is intensive research on the synthesis of monodispersed mesoporous TiO_2 spheres having the range of 100 nm to 12 μm based on the hydrolysis and condensation reaction pathway. This had been achieved in the medium of solvent and hydrolysing agent. Here the deciding factor for hierarchical morphology is the molar ratio between the Ti source and hydrolysizing agent. Ethanol/water is the most commonly chosen solvent and hydrolysing system and the most comprehensive analysis on this subject was carried out by

Hong et al. [44]. In order to obtain a uniform size distribution the formation nuclei should occur simultaneously in a short period of time. The growth rate and concentration of growth species should also be rapid in order to avoid further nucleation [45]. The formation of dual morphology nanomaterials in this present work can be obtained either from the slow growth rate (allowing more nucleation sites to form during the growth process) or when the concentration of growth species is less (which also allows for secondary nucleation to occur) [45]. In the formation of spheres with nanoparticles combination, the nuclei for the sphere shaped nanoparticles may be formed initially and further growth takes place over an extended time period. The process of growth is in such a way that it leaves precursors at a high enough concentration to create further nucleation and therefore both the processes could have happened simultaneously. Finally in the chosen environmental condition with precursor/hydrolysing solvent molar ratio nanospheres with nanoparticles mixtures was achieved. The addition of acetic acid in the water/ethanol system may speed up the process of growth rate or may help in aggregation of primarily nucleation sites in the shape of microspheres with the granules of nanoparticles. As it has acted as forward catalyst to increase the growth rate/aggregation of nucleation sites, further formation of nucleation sites are significantly reduced. In this way nanoparticles are formed on the surface of grown microspheres.

A higher number of primary/secondary nucleation sites occurs and the smaller aggregation results in florets of cauliflower-top-surface-like structures with irregular shaped nanoparticles formed in the presence of ammonia. Larger aggregation resulted in stone like structures. The evolutions of morphologies are given as the schematic diagram of Fig. 2.

3.2. X-ray diffraction analysis

X-ray diffraction analysis was carried out to identify phase formation and the crystallographic structure of the prepared samples. Fig. 3. shows the X-ray diffractograms of the synthesized powders. The X-ray diffraction peaks located at 2θ values of 25.3° , 38.6° , 48.1° , 53.9° , 55.1° , 62.8° , 68.8° , 70.4° , and 75.2° can be attributed to (101), (004), (200), (105), (211), (204), (116), (220) and (215) planes of the tetragonal structure of anatase phase TiO_2 with I41/amd space group symmetry (JCPDS Card No. 894921). No other peaks corresponding to secondary phases were detectable in the XRD pattern indicating the formation of pure anatase phase of synthesized samples. The sharp and intense reflection at (110) plane reveals the strong crystalline nature of the material, which may be favourable for electron transport. The lattice parameters a and c for all the synthesized TiO_2 samples are determined corresponding to the tetragonal structure using the following expression [46]:

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (1)$$

The calculated and standard d values with respect to their hkl planes for NSNP are given in Table 1. The standard and calculated lattice parameters for all materials are listed in Table 2.

Crystal sizes were calculated from the broadening of most intense (101) reflection using Debye Scherer's formula for all the samples [47]. The calculated crystalline sizes were found to be 12.21 nm, 12.95 nm, and 16.10 nm for NSNP, μ SNP, NSP respectively indicating that the addition of acetic acid and ammonia both results in increase in crystal size, which decreases the full width half maxima of the diffraction peaks.

3.3. Scanning electron microscopy analysis

The morphological features of prepared TiO₂ powders were examined using field emission scanning electron microscopy. Fig. 4. (a-c) presents the FESEM image of TiO₂ composites and (d-f) particle size distribution curves of corresponding FESEM images. Fig. 4. clearly indicates that addition of acetic acid and ammonia plays a significant role in morphological changes. Fig. 4(a) shows FESEM images of synthesized TiO₂ powders in water/ethanol binary solvent system. This dual morphology nanostructure consists of a proportion of spheres and nanoparticles which are well interconnected to each other. Spheres are in the average range of 170 nm in diameter. Fig. 4(b) represents the micrograph image of the sample on addition of acetic acid. It consists of microspheres. These microspheres have smooth surfaces and are composed of nanoparticles granules. These smooth surface microspheres are naturally well diffused to each other neck to neck among the growth species. Nanoparticles are decorated over the surfaces of these microspheres. As ammonia was used in addition to the binary solvent system of ethanol with water, the morphology of the sphere was affected greatly which was evident from Fig. 4(c) which resulted in another morphology due to the larger aggregation of nanoparticles. These stone like morphologies had smooth surfaces. The smaller aggregation of nanoparticles resulted in florets of cauliflower like structures of the order of less than 50 nm.

3.4. Transmission electron microscopy analysis

The structure and crystallinity of anatase TiO₂ were further investigated by high resolution transmission electron microscopy along with corresponding selected area electron diffraction pattern. Fig. 5(a) shows the HRTEM morphology of the synthesized NSNP TiO₂ powder. It confirms the presence of morphological features that are spherical shaped. Fig. 5(b) shows the SAED pattern of TiO₂ powder as spotty sharp ring pattern. The sharp ring pattern in selected area diffraction confirms the prepared TiO₂ are crystalline in nature. The lattice space values are calculated from diffraction rings of SAED pattern, the calculated lattice space values are 0.35 nm, 0.24 nm, 0.19 nm, 0.17 nm, 0.15 nm indexed to (101), (004), (200), (105) and (204) planes of anatase phase TiO₂. The SAED pattern analysis is in agreement with XRD measurements.

3.5. Laser Raman studies and phonon confinement model

Laser Raman spectroscopy has been employed to confirm the anatase phase TiO₂. The anatase phase belongs to the D_{4h}¹⁹ space group with two formulas per unit cell. Based on group theory the anatase TiO₂ consists of one A_{1g}, two B_{1g}, and three E_g modes as shown in **Fig. 6**. The Raman lines centred at 145cm⁻¹, 197cm⁻¹, 399cm⁻¹, 518cm⁻¹, and 639cm⁻¹ are attributed due to E_g, E_g, B_{1g}, A_{1g}, + B_{1g}, E_g, modes of anatase respectively [48]. **Fig. 7** depicts normalized experimental Raman spectra of 144cm⁻¹ mode.

The phonon confinement model (PCM) correlates the Raman scattering peak position and shape with size distribution effect of TiO₂ nanocrystals. When the phonons are confined in the case of small sized crystals contraction of translational symmetry occurs. Due to this the phonon wave function is expressed as a Gaussian confinement function instead of plane wave. The attention is focussed on the high intense E_g Raman active mode for the phonon confinement model. In the case of spherical nanocrystalline materials the Raman band intensity is proportional to the superposition of weighted Lorentizan contribution over the Brillion zone represented in the Eq. (2).

$$I(\omega) \propto \sum_{i=1}^2 \int \frac{e^{\left(\frac{-q^2 L^2}{2\alpha}\right)}}{\left(-\square_i(q)\right)^2 + \left(\frac{\Gamma_0}{2}\right)^2} d^3 q \rightarrow ()$$

Where

$$\square_1(q) = \square_0 + \square_1(1 - \cos(q \cdot a)) \rightarrow ()$$

$$\square_2(q) = \square_0 + \square_2(1 - \cos(q \cdot a)) \rightarrow ()$$

Here $\square_0 = 143 \text{ cm}^{-1}$ $\square_1 = 28 \text{ cm}^{-1}$ $\square_2 = 102 \text{ cm}^{-1}$ [37]. Γ_0 is the FWHM of the 143 cm^{-1} Raman peak for bulk anatase which is 7 cm^{-1} . q and a are the wave vector and lattice constant. The theoretical simulation was performed using simple phonon dispersion using representation given in equation (2) and (3) for the characteristics peak of anatase 143 cm^{-1}

Fig. 8. shows normalized simulated Raman spectra for different crystal sizes 12.21 nm, 12.95 nm and 16.10 nm calculated using Eqs. (2), (3), (4). The calculated Raman spectra using PCM provides evidence for the systematic shift towards the higher wave number side and a broadening of the FWHM with respect to a decrease in the nano crystallite size. It also agreed with an experimental observation given in Fig. 7. PCM reflects the influence of crystallite dimension on the lattice dynamics modification because PCM takes into account the contributions of phonons even away from the zone centre which result the shape variation in Raman line.

3.6 Two dimensional correlation analysis:

In order to perform an analysis of the shift of Raman band position with respect to particle size, the samples were analysed using two dimensional correlation spectroscopy. **Fig. 9** shows (a) synchronous and (b) asynchronous 2-D correlation spectra in the spectral range of $90\text{-}190 \text{ cm}^{-1}$ from the experimental Raman spectra. The synchronous spectrum develops a single autpeak at 145 cm^{-1} , while the corresponding asynchronous spectrum exhibits the standard butterfly pattern, which consists of a pair of cross peaks with opposite sign located at 143 and 148 cm^{-1} , respectively. The 1-D Raman spectra and 2-D synchronous spectrum divulge a single peak at 145 cm^{-1} whereas the corresponding asynchronous spectrum has two cross peaks at 143 cm^{-1} and 148 cm^{-1} , which indicates the shifting of band position. The direction of shift is determined by the sign of the peaks in the asynchronous spectrum. In **Fig. 10b** the cross peak above the diagonal line is positive and below the diagonal line is negative, which indicates the band position is shifting from higher a wavenumber side to lower wave number side [50].

Fig. 9 (c,d) shows the synchronous and asynchronous 2-D correlation spectra in the region of $300\text{-}700 \text{ cm}^{-1}$. The synchronous counter map develops three auto peaks at $640, 516, 397 \text{ cm}^{-1}$. While asynchronous cross peaks located at $637, 514, 396 \text{ cm}^{-1}$. The presence of three auto peaks represents the intensity variation occurs at different wave numbers. In addition to that the synchronous spectrum has positive cross peaks at $(640, 516) \text{ cm}^{-1}$, $(640, 397) \text{ cm}^{-1}$, and $(516, 399) \text{ cm}^{-1}$ indicating that a decrease in intensity in the pair of bands occurs in same direction. The observation from synchronous and asynchronous 2-D correlation analysis indicates that all the above indicated peaks are shifted to the lower wave number side as a function of increasing particle size [51].

3.7. UV-Vis spectra analysis

The light scattering abilities of photoanodes plays a critical role in the efficiency enhancement of DSSC. Scattering occurs, when the electromagnetic radiation meets the particles whose sizes are comparable to the wavelength of the light. Photons are scattered either in a diffused form or in the specular form. The DSSC takes advantage of diffused reflectance. The diffused reflectance increases the optical path length of the incident photon inside the medium of TiO₂. After sensitization the TiO₂ medium gets associated with the grafted sensitizer molecules. Hence the probability of interaction increases between the sensitizer molecules with photon which leads to an increase in photon absorption. Hence, the light scattering abilities of the screen printed photoanodes without dye loading can be recognized by UV-vis diffused reflectance spectra, which is a good indicator to the performance of the material in the PV device.

The NPS exhibited higher diffused reflectance for the entire visible region starting from 350 to 800 nm. The differences between the DRS of the photoanodes screen printed by the NSNP, μ SNP with respect to NPS are clearly visible from the Fig. 10. Fig. 11 shows the UV-vis absorption spectra of photoanodes after dye sensitization process. Fig. 11 clearly indicates that NPS demonstrated the highest absorption among all the synthesized dual morphologies. All the samples comfortably agreed with the diffused reflectance measurement results. Superior performance of NPS among the three samples may be due to higher surface area for more dye loading and higher diffused scattering ability. Higher dye loading capability of the NPS is due to the higher density of smaller available nanoparticles in the NPS. Fig. 4(c) shows that small numbers of particles are more numerous. When compared to other two samples NPS also has a denser packing as seen in the FESEM micrographs. This is also further supported by the particle size distribution curves. In Fig. 4(b) diffused microsphere contents are more in proportion when compared to the nanoparticles proportions. Even though the NSNP has higher proportion of nanoparticles as compared to its constituent spherical morphology, the density of particle packing in the obtained structures may be less compared to NPS. Hence, the diffused reflectance and optical absorption strongly agreed with the above interpretation of the morphology content.

3.8 .Photovoltaic performance of DSSCs

Fig. 12a represents a schematic device configuration and working mechanism of dye the sensitized solar cell. The photons from the sunlight strikes the dye molecules anchored on semiconductor photoanode. The electrons excited by the energy of photon will be injected from the lowest unoccupied molecular orbital of sensitizer to the conduction band of TiO₂ when the potential of conduction band matches with LUMO of sensitizer. Here the injected electron travels through the thickness of the TiO₂ layer within its life time. These electrons reach the conductive substrate of FTO in the working electrode and from here go to the counter electrode through the load. Meanwhile regeneration of sensitizer should take place in order to maintain stability otherwise the whole system could not continue its operation by dye degradation. Here the redox mediator of I⁻/I₃ couple supply electrons for the oxidised sensitizer to bring it to its neutral state. In this way the process again starts from the initial point in order to continue the DSSC cycle.

The photovoltaic performance were analysed by measuring the current–voltage curves under one sun illumination. **Fig. 12b** shows the current density–voltage curves of three photoanodes and corresponding photovoltaic parameters are listed in **Table 3**. The photo anode A shows highest short circuit current density (J_{SC}) of 11.48 mA/cm^2 , open circuit voltage (V_{OC}) 0.66 V and overall power conversion efficiency 4.17% . Sample B and sample C exhibits the DSSC efficiency as 2.64% and 3.04% , respectively. Sample B has a nature of the highest diffused light reflectance and more dye loading even though, it offers lower power conversion efficiency compared to sample A.

In general, the reported results agree with the UV-Vis diffused reflectance and absorption results. That is the highest diffused reflectance and the dominant absorption exhibited by the photoanodes had been shown higher efficiency in DSSC [52], but in the present investigation the obtained results of photovoltaic performance do not show the linear relationship with our UV-Vis diffused and absorption measurement. Hence, a more in-depth analysis of electron transport properties of photoanodes is provided below.

3.9. Electrochemical Impedance analysis

In order to investigate the charge transfer resistance and recombination properties of photo anodes electrochemical impedance spectra (EIS) measurements were carried out for the fabricated DSSC under dark condition. **Fig. 13 (a)** represents the Nyquist plots for three different photo anodes DSSCs. The impedance data of the DSSCs were fit by the equivalent circuit using ZView software and corresponding EIS parameters are summarized in **Table 3**. An equivalent circuit consisting of series resistance (R_s), charge transfer resistance (R_{ct}) and constant phase element (CPE) offer the best fit for impedance plots. Generally a semicircle with large radius of curvature in the Nyquist plot is ascribed to the electron transport phenomenon across the interface of TiO_2 /dye/electrolyte. In addition to that it also accounts the electron transport within TiO_2 layer. From **Fig 13 (a)** the Nyquist plot of sample A possess smallest diameter. It reveals the device based on sample A offers the lowest R_{ct} value when compared with the DSSC device based on photoanodes B and C. This lower charge transfer resistance of photoanode A could be attributed to the efficient charge transfer process and slower electron-hole recombination which leads to the best photovoltaic conversion efficiency. It may due to either it offers lower interface charge transfer resistance across working electrode/ Dye/ electrolyte interface or nanoparticles cum nanosphere structure may provide large number electron path ways for fast electron transport and diffusion of electrolyte.

Comparatively less photovoltaic performance of sample C with sample A may due to the huge number of trapping in the grain boundaries or lacking of enough diffusion of redox couple leads for higher R_{ct} , which restricts the power conversion efficiency of DSSC. Hence the electrochemical measurements strongly supported the results obtained from photovoltaic measurements results.

4. Conclusions

TiO_2 dual morphology composite structures were successfully synthesized and demonstrated for use in DSSCs. Out of the three different dual morphologies prepared by a simple less time consuming procedure the material consisting of nanospheres with nanoparticles exhibited a higher solar conversion efficiency. Even though the dual morphology of nanoparticles with stone like structure exhibited higher scattering ability and more optical absorption it showed non linearity with power conversion performance in DSSC. This phenomenon is discussed with experimental evidence obtained from

electrochemical impedance measurements. In conclusion the improved power conversion efficiency of nanospheres with nanoparticles have the dual role of providing optimum surface area for dye loading and acting as light scattering centres. These properties when optimized along with the offered pathway for electrolyte diffusion to the dye degeneration with less charge transfer resistance could lead to better photoelectric conversion efficiency.

Acknowledgements

We gratefully acknowledge the financial support and screen printing facility from Government of India, DST-SERB research grant under the project SR/FTP/PS-012/2011. The author JM is thankful to the UGC-UPE and DST-PURSE, MKU for the I-V measurements. JMP would like to thank the Richard Witte Endowment for Materials Science and Engineering for support of this work.

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Hydrolysis

Condensation

Fig. 1. Schematic diagram of hydrolysis and condensation reaction of TiO₂

Fig. 2. Schematic diagram of evolution of nanocomposites.

Fig. 3. The XRD pattern of prepared dual morphology TiO₂ powders

Fig. 4. FE-SEM images of the prepared dual morphology TiO₂ materials (a) A (b) B and (c) C .(d-f) particle size distribution curve from FE-SEM images.

Fig. 5.(a) TEM micrograph of sample A (b) SAED pattern of TiO_2 .

Fig. 6. Raman spectra of TiO₂ powder samples

Fig.7. Normalized experimental Raman spectra of 144cm^{-1} mode for prepared dual morphology TiO_2 powders.

Fig. 8. Simulated Raman Spectra using phonon confinement model as a function of particle sizes at 144cm^{-1} mode.

Fig. 9. (a) synchronous, (b) asynchronous 2D correlation spectra in the spectral range of 90-190 cm⁻¹ and (c) synchronous, (d) asynchronous 2D correlation spectra in the region of 300-700 cm⁻¹.

Fig. 10. Diffused reflectance spectra of photoanodes before dye loading.

Fig. 11. Absorbance spectra of A, B and C photoanodes after the dye uptake process.

Fig.12.(a) Schematic device configuration and working mechanism of dye sensitized solar cell. (b) Current density-Voltage curve for different photoanodes.

Fig. 13. (a). Nyquist plot representation of DSSCs based on A, B and C photoanodes under dark conditions, (b) Equivalent circuit model of fabricated DSSC.

(c)

Table 1. Angle of diffraction corresponding lattice planes of standard and calculated d-spacing values of Sample A.

2 θ	(hkl)	d _{std.} (Å)	d _{cal.} (Å)	Δd (Å)
25.35	(101)	3.509	3.516	0.007
38.64	(112)	2.328	2.331	0.003
48.14	(200)	1.888	1.892	0.004
53.97	(105)	1.697	1.699	0.002
55.18	(211)	1.663	1.666	0.003
62.81	(204)	1.478	1.480	0.002
68.87	(116)	1.362	1.363	0.001
70.45	(220)	1.335	1.337	0.002
70.20	(215)	1.262	1.264	0.002

Table 2. The standard and calculated lattice parameters a, c and corresponding crystalline size of all the TiO₂ materials.

Samples	Crystalline Size (nm)	Lattice parameters (standard) (Å)		Lattice parameters (observed) (Å)	
		a	C	A	c
A	12.21	3.777	9.501	3.765	9.411
B	12.95			3.769	9.449
C	16.10			3.771	9.481

Table. 3. Photovoltaic and EIS Parameters derived from fabricated DSSC devices.

Sample	J _{SC} (mA /cm ²)	V _{OC} (V)	FF	η (%)	R _s (Ω)	R _{CT} (Ω)
A	11.49	0.66	0.54	4.17	37.0	45.4

B	7.24	0.68	0.53	2.64	24.2	87.0
C	7.78	0.69	0.55	3.04	36.0	46.0