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MORPHOLOGICAL IMPACT OF TiO_2 NANOSTRUCTURES ON TRANSPORT PROPERTIES

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Abstract-Dye Sensitized Solar Cells (DSSCs) implanted with morphologically modified nanostructures are receiving great attention owing to their efficient transport of photo generated carriers, whose employment is expected to improve the cell performance. Herein, we report a facile hydrothermal method to synthesized TiO_2 film composed of nanorod-arrays and nanopowder composed of flowers-like nanorod-arrays. The as-synthesized samples were characterized by Field Emission Scanning Electron Microscopy (FESEM), X-Ray Diffraction (XRD), Ultra Violet-Visible Spectroscopy (UV-Vis) and Photoconductivity techniques. FESEM textural properties revealed densely aligned nanorod like structure in the case of TiO_2 film, whereas bud like cluster-nanorods manifested with nanoflower morphology in the TiO_2 powder. The X-ray Diffraction (XRD) analysis indicated that both the structures conform rutile TiO_2 phase with an average crystallite size of about 13.86 and 33 nm respectively. From the UV–Vis absorption spectra, it was evident that the absorption of TiO_2 nanoflowers in the UV region was significantly higher than TiO_2 nanorods. The flower-like nanostructure possessed superior photoconductivity as a consequence of its lower optical band gap and larger surface area thus presenting them as proficient photoanodes for DSSCs.

Keywords: Morphology, Nanostructures, Transport Properties, Hydrothermal, Photoconductivity

I. INTRODUCTION

Energy has been a part of our life; especially electrical energy plays a vital role in our modern society. With ever-increasing population rates, energy demand has also been increasing at an escalating speed over the past few decades. To meet the increased demand, every country has started to explore different energy systems to produce and store electricity in an efficient and most importantly an eco-friendly way [1]. Due to the progress of nanotechnology, nano-sized structures can be created that could boost energy storage and solar cell performance [2-3].

Synthesis of nanocrystals with exposed high-energy facets is a well-known challenge in many fields of science and technology [4]. Recently, it has been widely reported that TiO_2 nano structures enhance performance in photocatalysis, dye-sensitized solar cells [5], and lithium-ion batteries [6] particularly due to the exposed surfaces and unique anisotropic structures [7]. Titanium dioxide (TiO_2) is a well-known wide-band gap semiconductor which has been investigated as an excellent photocatalyst, owing to its outstanding properties such as non-toxicity, low cost, and long-term stability [8-9].

Among the different shapes of TiO_2 one dimensional (1-D) nanostructures including nano-wires, nanorods as well as nanotubes [10] and 3-D nanostructures such as nanoflowers have aroused substantial research interest not only because of their specific quantum-confinement effects but also due to their ability in conducting electrons, which make them very promising for future applications in nanoelectronics and photovoltaic cells [11]. Usually the formation of TiO_2 nanorods can be used as efficient electrical pathways for the generated charge carriers because of high electrical mobility [12-13]. TiO_2 nanoflowers have high specific surface, large light-harvesting efficiency and also exhibit high photocatalytic activity [14].

In the present investigation we focus on the investigation of hydrothermally synthesized rutile TiO_2 nanorod films coated on Indium Tin Oxide (ITO) and flower-like nanorods in the powder form.

II. METHODOLOGY

Hydrothermal method, one of the traditional methods for crystal growth of semiconductors, is frequently used to prepare TiO_2 [15] owing to its effective reaction in environment with stable temperature and pressure. It is a simple method because of its easy preparation, control of particle size and cost effectiveness [16]. Therefore, hydrothermal process is a promising approach to prepare well aligned nanostructures in large scale [17].

A. Synthesis of TiO_2 nanorod films

The TiO_2 nanorod arrays were synthesized by hydrothermal method following the procedure described herein. The ITO conducting substrates were ultrasonically cleaned with acetone and deionised water in sequence, for 10min prior to the coating process. A mixed solution which was obtained by adding 25mL of deionized water to 20mL of concentrated hydrochloric acid was stirred for a few minutes using a magnetic stirrer. An amount of 0.2mL of Titanium tetrachloride ($TiCl_4$) was added to the above solution and stirred further. Before the hydrothermal reaction, pretreated ITO substrate was placed inside the Teflon vessel with its conductive side facing downwards. The as-prepared solution was then transferred into the Teflon vessel, was sealed in a stainless steel autoclave and heated up to 180^0C for 2 hours. After hydrothermal reaction, the autoclave was cooled down quickly to room temperature. The samples thus obtained were rinsed with deionized water. The as-synthesised TiO_2 film was then dried in ambient air [18].

B. Synthesis of TiO_2 nanoflower like powder

The flower like rutile TiO_2 nanostructures were also fabricated by a similar hydrothermal reaction. Firstly 1mL of titanium butoxide was added drop wise to 60mL of a magnetically stirred mixed solution containing deionized water and hydrochloric acid (1:1). After stirring for 15 min under room temperature, the solution was transferred to a Teflon vessel. The Teflon vessel was then sealed in a stainless steel autoclave and maintained at a temperature of 190^0C for 18 hours. After natural cooling down, the products were collected by washing with de-ionized water and ethanol to remove any residual reagents and organic solvents. After drying at 60°C, the resulting powder was annealed at 700 °C to obtain TiO_2 nanoflowers [19].

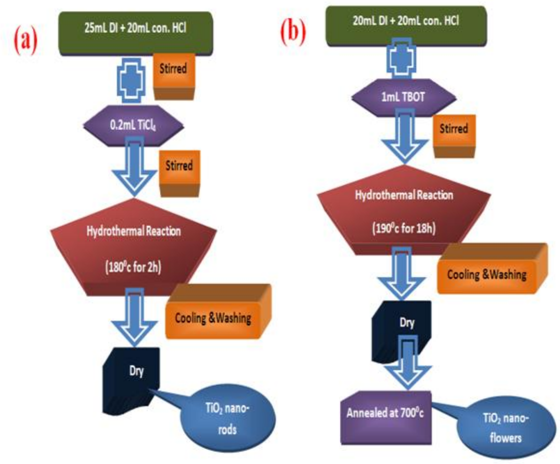

Fig 1 Flow Chart for preparation of TiO_2 (a) Nanorods and (b) Nanoflowers

C. Characterization

The surface morphology of the sample was recorded by a Field Emission Scanning Electron Microscope (FESEM: SUPRA-55 Carl Zeiss and FEI Quanta FEG 200 equipped) [20]. X-ray diffraction (XRD) [21] measurements were carried out using Rikagu, Japan and RICH SEIFERT X-Ray Diffractometers with CuKα radiation (λ = 1.5406A°) and used to analyze the crystalline structure [22]. The UV-Vis absorption spectroscopy [23] was done by CARY5 spectrophotometer at room temperature in the range 200-800nm. Field dependent dark and photoconductivity characteristics were recorded using Keithley pico-ammeter 6485 by an indigenous set-up devised at our own Research Laboratory, ENTeC-LIFE and reported by Ponniah and Xavier [24].

III. RESULTS AND DISCUSSIONS

A.Surface Morphology

The FE-SEM images of the as-prepared TiO_2 thin films (Fig 1 (a) and (b)) shows densely aligned nanorod structures [25-26]. The average length of the nanorods is 447 nm. As seen in Fig 1(c) and (d) the morphology of the TiO_2 powder represent bud like cluster-nanorods manifested as nanoflowers [27-28].

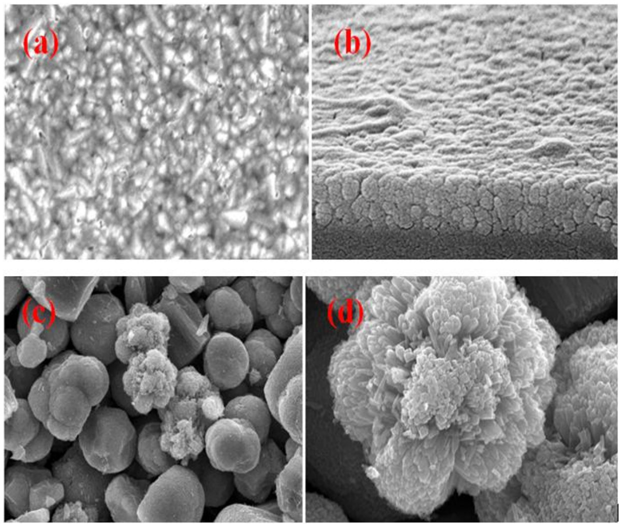

Fig 2 FESEM images: (a) an overview of TiO_2 nanorods (b) compactly aligned nanorods (c) bud-like nanorod clusters and nanoflowers and (d) a closer view of a nanoflower composed of nanorods

The 1D nanostructures were highly crystalline and this is expected to enhance the electron transport properties by providing a direct pathway for electrons within the aligned morphology. Unfortunately, the performance of the 1D nanostructures based solar cells do not reach the expected value because the surface area of the 1D nanostructures usually turned out to be much smaller than that of conventional mesoporous structures. Further enhancement of the solar cell efficiency could be realized by the development of 3D hierarchical nanostructures by adding extra dimensions to the vertically aligned 1D nanorods arrays with such structures as nanoflowers, nano-trees, nano-forests, nano-dendrimers etc. [29].

B. Structural Properties

Fig 2 (a) and (b) show the XRD patterns of nanorod films and nanoflower powder samples respectively. The diffraction peaks of the thin film and powder structures agree to the pure rutile phase (JCPDS No: 03-065-0191 and021-1276). Distinct diffractions such as (110), (101), (111), (210), (211) , (211), (002), (221) ,(301) and (112) at 27.58°, 36.23°, 41.41°, 44.20°, 54.49° 54.7^0, 61.5^0, 65.9^0, 69.18° and 72.9^0 respectively, are clearly noticeable [30-31]. The samples are well-crystallized in the rutile phase of TiO_2. It is well known that rutile polymorph exhibits some superior physical properties such as enhanced light-scattering properties on account of its higher refractive index, effective light harvesting [32-33]. The average crystalline size of the sample was calculated using the Scherrer's formula [22]. Both XRD patterns show the presence of a broad XRD peak at 61.5^0 and 62.93°, which was an indication of crystallite size of 13.86 and 33 nm respectively.

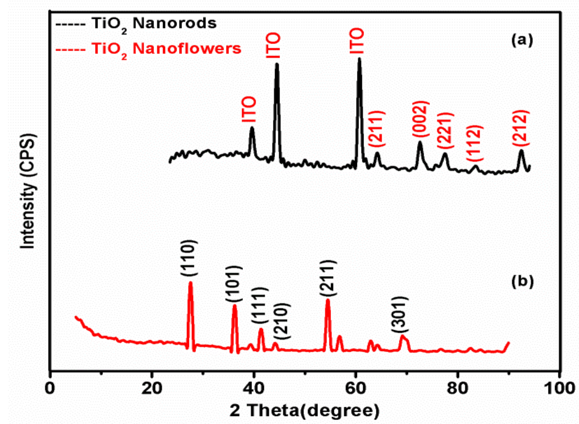

Fig 3 XRD images of Rutile-TiO_2 (a) Nanorods and (b) Nanoflowers

C. Optical Absorption

The UV-visible absorption spectra of the TiO_2 rods and flower-like nanostructure are shown in Fig. 4 (a) and (b) show the absorption spectra of the samples and they indicate that the absorption of the flower-like TiO_2 nanopowder is stronger than that of TiO_2 nanorods film. The flower-like nanostructured sample recorded a strong optical absorption peak at 365 nm and nanorod sample had an optical absorption peak centered around 300-330 nm. This may be due to the fact nanoflower TiO_2 structures are basically composed of nanorods, which present high specific surface area, high electrical mobility and large harvesting ability of light due to multiple scattering of light within the nanostructure framework [14]. It is also reported that surface area and surface defects play important roles in the photocatalytic activities of metal oxides. Additionally, they affect the optical and electronic properties due to which the optical absorption shifts towards the visible region. It is a recommended absorption value for achieving a visible-light active photocatalyst. This is important because of the fact that the solar spectrum has only < 7% UV energy and more than 50% visible energy [34]. Therefore, the photocatalytic activities of flower-like TiO_2 nanostructures would be higher than that of TiO_2 nanorods.

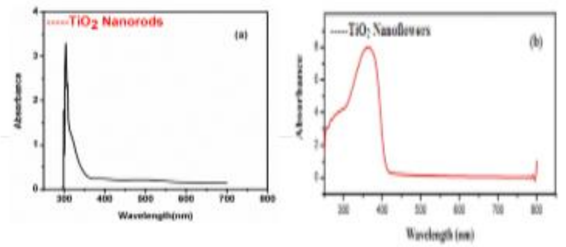

Fig 3 UV-Visible absorption spectra images of TiO_2 (a) Nanorods and (b) Nanoflowers

D. Photoconductivity

The plot in Fig.5 indicates a linear increase of current in the dark and visible light illuminated samples with increasing applied field there by depicting the ohmic nature of the contacts. Based on the results obtained from the UV-visible absorption spectra, the variation of dark and photoconductivity of flower-like TiO_2 nanostructure was alone analyzed. It was observed that the photocurrent (I_P) was significantly greater than the dark current (I_D) in the TiO_2 nanoflowers. The flower like nanostructure arrangement has very large surface area for light absorption with oxygen interaction and size dependent properties, such as increased photo-absorption, transport of charge carriers and dye-absorption. This is vital, as the structured part of the light-absorbing material is the surface in direct contact with the dye molecules. This study therefore evidences that rutile-phased TiO_2 nanoflowers possess the ability to enhance the dye-absorption property as they showcase improved photoconductivity [35].

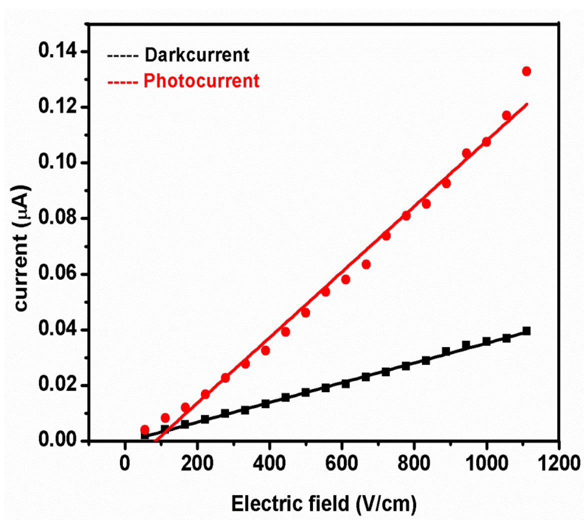

Fig 5 Field dependent conductivity of TiO_2 nanoflowers

IV.CONCLUSIONS

Rutile TiO_2 with complex nanostructures, such as nanorods and nanoflowers can be synthesized by using a facile hydrothermal method with different precursor materials. FESEM image revealed densely aligned nanorod in the film and bud like cluster-nanorods manifested with nanoflower morphology in the TiO_2 powder. The X-ray Diffraction (XRD) analysis indicated that the nanorods and nanoflowers possessed average crystallite sizes of about 13.86 and 33 nm respectively. From the UV–Vis absorption spectra, the absorption of TiO_2 nanoflowers in the UV region was found to be significantly larger than the TiO_2 nanorods. Accordingly the nanoflowers showcased improved photoconduction thus predicting that they could serve as good mediators for transport properties. The findings point out that the morphology of the nanostructures bear an impact on their optical performance thereby suggesting TiO_2 nanoflowers as proficient photoanodes for DSSCs.

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