



Research Article

Schottky junction based solar cell behavior of trichome hierarchical SnO₂ nano-structuresG. Mallik^a, A. Kabiraj^a, P.P. Dash^a, P. Kumari^a, Utkalika P. Sahoo^b, P.K. Sahoo^b, S. Rath^{a,*}^a Nano-Structure and Soft-Matter Physics Laboratory, School of Basic Sciences, Indian Institute of Technology Bhubaneswar, Jatni, 752050, Odisha, India^b School of Physical Sciences, National Institute of Science Education & Research (NISER) Bhubaneswar, an OCC of Homi Bhabha National Institute, Jatni, 752050, Odisha, India

ARTICLE INFO

Keywords:

Tin dioxide (SnO₂)
 Trichome nano-flowers
 Hierarchical nano-structures
 Optical properties
 Schottky junction
 Solar cell

ABSTRACT

Hydrothermally grown SnO₂ hierarchical trichome nano-flowers (T-NFLs) have been examined for their device performance compared to nano-flakes (NFs), in part to meet the growing need for metal-oxide based solar cells. The structural analyses reveal superior lattice strain and free energy in the tetragonal phase of the T-NFLs over NFs. The band gap widening and oxygen defect-dominated luminescence in the visible range are observed from photoluminescence measurements. Compared to NFs, the Schottky current-voltage characteristics of the T-NFLs show improved Schottky barrier height (0.82 eV) with an ideality factor of 3.52 under dark and better solar cell properties with a conversion efficiency of $1.78 \pm 0.03\%$ under 1 sun illumination. The observed high open-circuit voltage of 1.56 V resulted from the decrement rate of carrier recombination, making the transparent metal oxide nano-material SnO₂ T-NFLs suitable for solar cells and fast electronic applications.

1. Introduction

Metal-oxide (MO) nano-structures with size hierarchical properties are promising for nano-devices applications [1–4]. In the presence of a nano-dimensional MO interlayer, the Schottky barrier diode (SBD) shows an advantage over device performance by reducing the “barrier height effect” [5–7]. As observed by A. Baltakesmez et al., the zinc oxide (ZnO) interlayer makes the SBD tolerant in a radiation environment [8]. The graphene-oxide interlayer facilitates the device with an enhanced resistive switching effect [9], barrier height modulation [10], and overcomes the contact limitations [11], etc. Among the MO, Tin dioxide (SnO₂) is a well-known transparent conducting oxide (TCO) material [12,13] with co-existing metallic–semiconducting [14] behavior due to the flexible and degenerate band structures [15,16]. As an interface layer, the TCO stabilizes the SBD by enhancing barrier characteristics [9], prevents cross-contamination between active layers [17], and eases the transmission of electrical current and light flow through the devices [18]. The SnO₂ nano-material with various physical shapes, viz., nano-rods, nano-sheets, nano-belts, nano-flowers, and nano-flakes, exhibit emerging field-emission properties, active electron transport layer (ETL), high-temperature photoconductivity, super-capacitor, and photo-catalytic behaviors, respectively [19–24] due to the quantum

confinement effect. Therefore, the size hierarchical SnO₂ nanostructures are significant for technological implications. In addition, unlike p-n junction-based solar cells, SBD-based solar cells have reduced manufacturing complexity [11], improved radiation resistance [8], lower dark current [25], low forward voltage [7], and minimal loss caused by carrier recombination [26]. Therefore, the TCO-based SBD cells are appropriate for light harvesting across a wide range of wavelengths, enabling greater power conversion efficiency. At the same time, the crystalline structures of the MO influence charge transport [6], which ultimately determines the efficacy of the devices. Hence, the comprehension of the size-induced enhanced electrical response of SnO₂ nano-structures under photoexcitation is inevitable to establish SnO₂-based electronic devices.

This report describes (i) the growth of shape-hierarchical SnO₂ nano-structures (nano-flakes to trichome nano-flowers) through hydrothermal technique followed by structural characterization and property evaluation; (ii) intriguing transitions dominated luminescence in the visible range are revealed by optical measurements; and (iii) the shape-hierarchical SBD current-voltage characteristics have been investigated to explore the TCO based solar cells.

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Received 6 June 2023; Received in revised form 21 August 2023; Accepted 25 August 2023

Available online 6 September 2023

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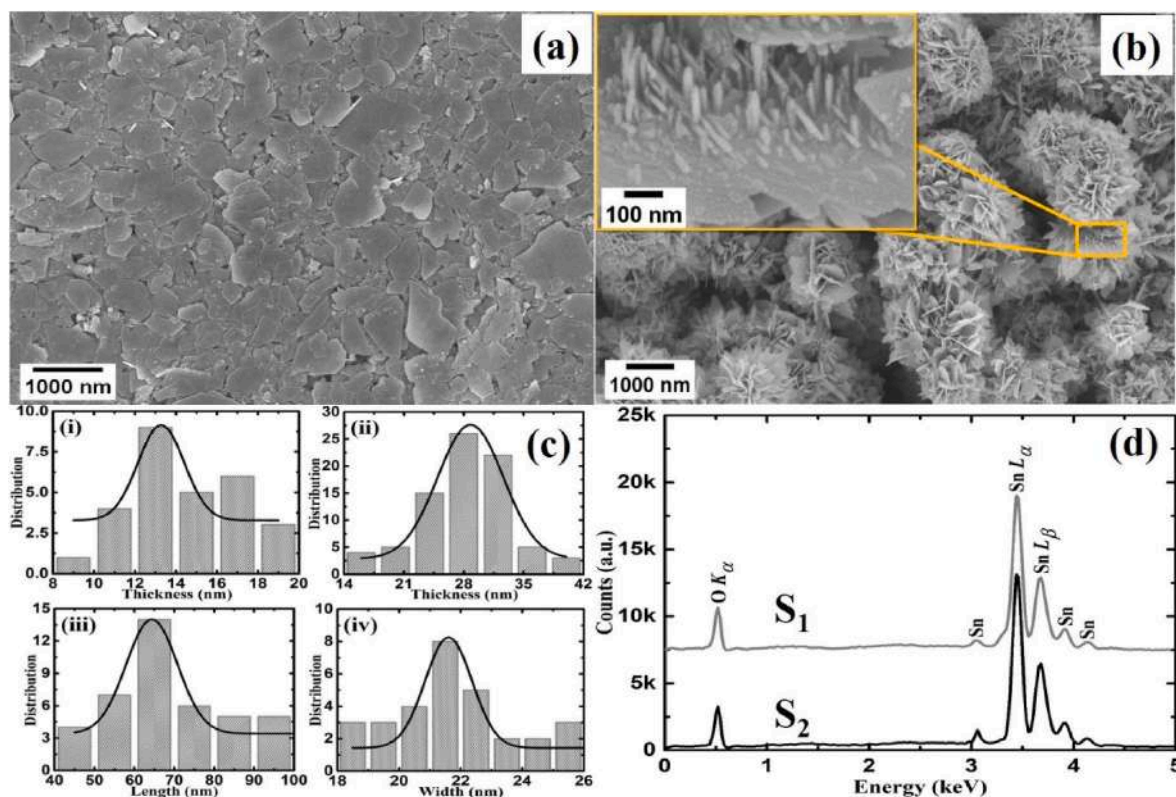


Fig. 1. FESEM micrographs of S_1 (a), S_2 (b) with the inset showing the growth of trichomes on the petals of the nano-flower structures. The thickness distribution histograms with Gaussian fittings (black solid curves) of S_1 (c) (i), S_2 (c) (ii), the length (c) (iii) and width (c) (iv) distributions with Gaussian fittings (black solid curves) of the trichomes. The EDS spectra of (d) S_1 (grey solid curve) and S_2 (black solid curve).

2. Experimental

The synthesis of size-hierarchical SnO_2 nano-materials is based on the alkali ion activated hydrothermal growth. The typical synthesis protocol consists of the following steps: (1) 0.25 M homogeneous $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ solution was taken in a 200 ml reagent bottle and heated at 393 K; and (2) 0.4 M KOH or 0.4 M NaOH solution was added dropwise to the above solution under vigorous stirring conditions during heating. (3) The resultant precursors were transferred to a 100 ml Teflon autoclave and heated at 453 K for 15 h, followed by natural cooling to room temperature (300 K). Two optimized samples, S_1 and S_2 , were prepared using KOH and NaOH as alkali-ion stimulated reducing growth agents, respectively. Then, the final solution was cleaned with double-distilled deionized water and ethanol using a centrifuge. The precipitate was dried in a vacuum for 24 h, yielding the sandy-brown-colored SnO_2 nano-structure powders.

The structural and compositional behavior of the SnO_2 nano-structured samples were analyzed using Merlin Compact (Gemini-I electron column), Carl Zeiss, Germany, field emission scanning electron microscope (FESEM), and Oxford Instrument, energy dispersive x-ray spectroscopy (EDS), respectively. To carry out the FESEM and EDS experiments, the water-dispersed samples were spin coated on cleaned silicon wafers. The x-ray diffractometer (XRD), Bruker D8 Advance diffractometer ($\text{Cu } K_{\alpha}$, $\lambda = 1.5418 \text{ \AA}$ [27]), operating at 40 kV and 40 mA, was used to investigate the crystal structures of the samples. The reproducibility of the growth process has been confirmed from FESEM, EDS, and XRD studies of several batches of samples. The Raman instrument, LabRam HR Raman instrument coupled with a CCD detector having 0.52 cm^{-1} spectral resolution, was utilized for the collection of Raman signals. The wavelength of 532 nm with power 30 mW from the He-Cd laser source was used as the Raman excitation line. Bruker α Alpha-T FTIR instrument was utilized to record the FTIR absorption

spectra of the samples. The photoluminescence (PL) analysis has been carried out using Agilent Cary Eclipse Fluorescence Spectrophotometer. The Shimadzu UV-1800 Spectrophotometer was used to study the spectral absorption characteristics of the samples.

The electrical properties of the samples were characterized by constructing four junction devices: Au/S_1 (D_1), Au/S_2 (D_2), (Indium Tin Oxide) ITO/S_1 (D_3), and ITO/S_2 (D_4). To construct D_1 and D_2 , metallic gold (Au) was sputter coated on a cleaned silicon dioxide (SiO_2) substrate using Quorum SC7620 sputter coating unit, followed by spin coating of the samples (S_1 or S_2). Similarly, the devices D_3 and D_4 were prepared on commercially available ITO substrates (thickness 200 nm), keeping other parameters constant. Here, the samples were spin coated at a rpm (rotations per minute) of 1200 for a duration of 3 min. Finally, using masking technique, silver (Ag) finger electrodes of thickness 200 nm and a total area of 0.03 cm^2 were sputter coated on the devices having total area 0.722 cm^2 . The use of finger electrodes facilitates the transmission of light through the TOC for photovoltaic effects in place and avoids the impact of heterogeneity in sample distribution over the active layers. The transport properties of the devices D_1 , D_2 , D_3 , and D_4 were analyzed using ScienceTech AAA Solar Simulator coupled with Keithley 2450 source meter. The devices were illuminated using a xenon lamp source in the presence of a 1.5 a.m. (air mass) filter. The reproducibility of SBD device behavior has been verified over a series of 10 samples from each batch.

3. Results and discussion

Fig. 1(a) and (b) are the FESEM micrographs of samples S_1 and S_2 respectively. From detailed analysis, it has been observed that sample S_1 exhibits nano-flake (NFs) structures, while S_2 exhibits nano-flower (NFLs) structures. At the same time, the inset of **Fig. 1**(b) reveals the growth of nano-rods on the surface of the petals of nano-flowers. These

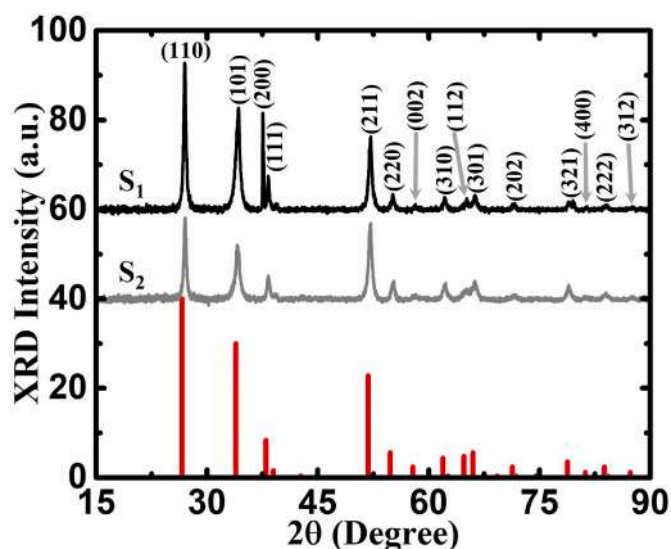
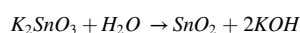
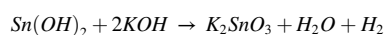
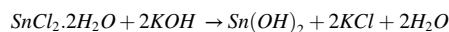


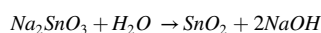
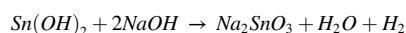
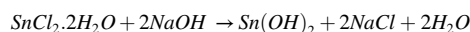
Fig. 2. XRD patterns of S_1 (black solid curve) and S_2 (grey solid curve), with the red colored bar plot indicating the peak positions and relative intensities of the standard JCPDS # 00-041-1445 data file.

studies yielded interesting nano-trichomes (i.e., upright nano-rods grown on the petal like structure) hierarchical nano-flower (T-NFLs) growth of S_2 in contrast to the nano-flake structure of sample S_1 . From the size distribution analysis as shown in Fig. 1(c-(i) & (ii)), the mean thickness of nano-flakes and the mean petal thickness of nano-flowers were found to be 13.28 nm and 28.79 nm respectively. The average size of trichomes is estimated to be 64.38 nm (Fig. 1(c-(iii))) having

width of 21.61 nm (Fig. 1(c-(iv))). The growth mechanism of trichomes hierarchical nano-flowers can be understood as follows. According to K. Sato et al. [28] and M. Guan et al. [29], the alkali-ion stimulated dissolution-precipitation reaction followed by in-situ crystallization [30] facilitates one-dimensional and two-dimensional growth. Further, it has been observed that by controlling the strength of interaction (e.g., the chemical reactivity of Na^+ ions (ionic radius ~ 0.19 nm) is greater than K^+ ions (ionic radius ~ 0.22 nm)) [31] and the concentration of alkali medium [29], a competitive reaction between dissolution-precipitation can be achieved, which facilitates for nano-flakes and nano-rods growth. Interestingly, the oxygen vacancy ridden crystallographic anisotropy present in the structure of the samples imposes additional hydrophobic-hydrophobic and hydrophilic-hydrophilic interactions that trigger a new dimensional growth process [28]. The chemical reactions involved in our synthesis protocol of samples S_1 and S_2 can be written as:



and



Here, the intermediate compounds potassium stannate (K_2SnO_3) and sodium stannate (Na_2SnO_3) are responsible for the typical growth of samples S_1 and S_2 due to the following interactions. The hydrophilic K_2SnO_3 is readily soluble in polar solvents, whereas the solubility of

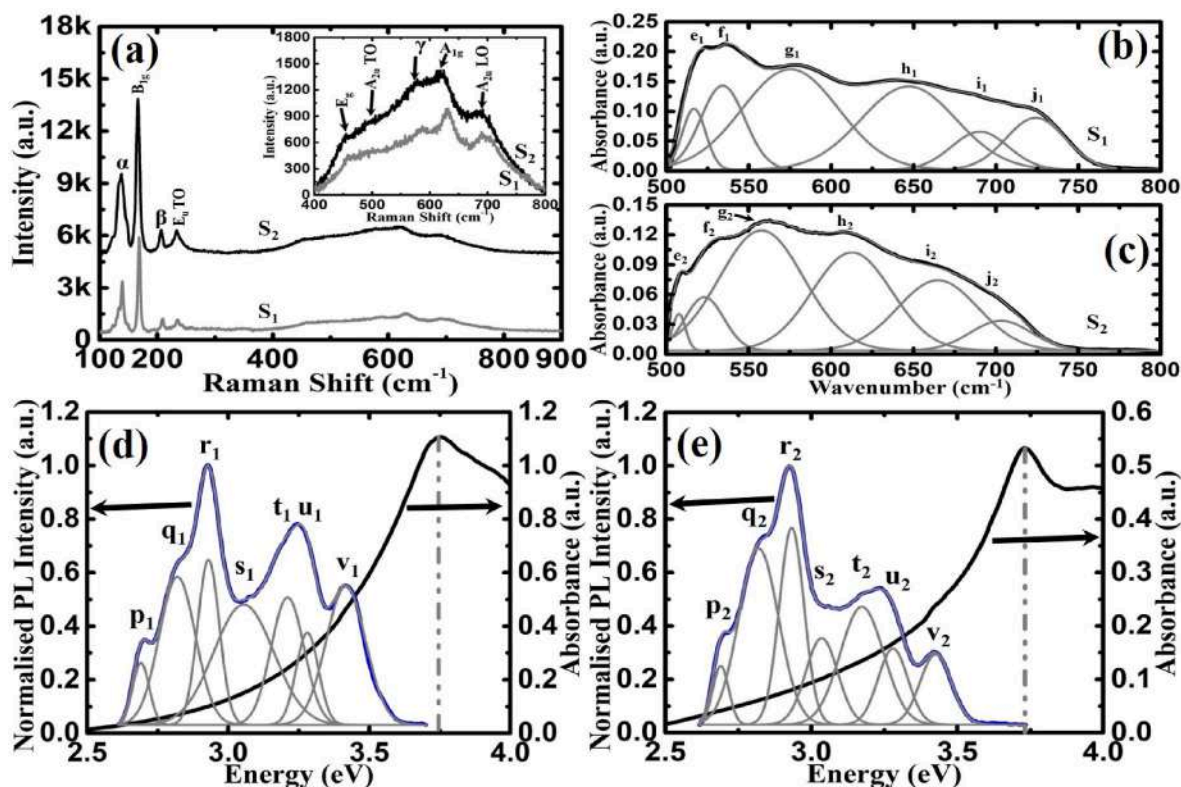


Fig. 3. Raman spectra (a) of S_1 (grey solid curve) and S_2 (black solid curve), with the insets depicting the magnified clear peak patterns of S_1 (grey solid curve) and S_2 (black solid curve) for the range 400 cm^{-1} to 800 cm^{-1} . The FTIR absorption spectra (black solid curve) with deconvoluted Gaussian peaks (grey solid curves) of S_1 (b) and S_2 (c). The PL emission spectra (blue solid curve) with deconvoluted Gaussian peaks (grey solid curves) and UV-vis absorption spectra (black solid curve) of S_1 (d) and S_2 (e).

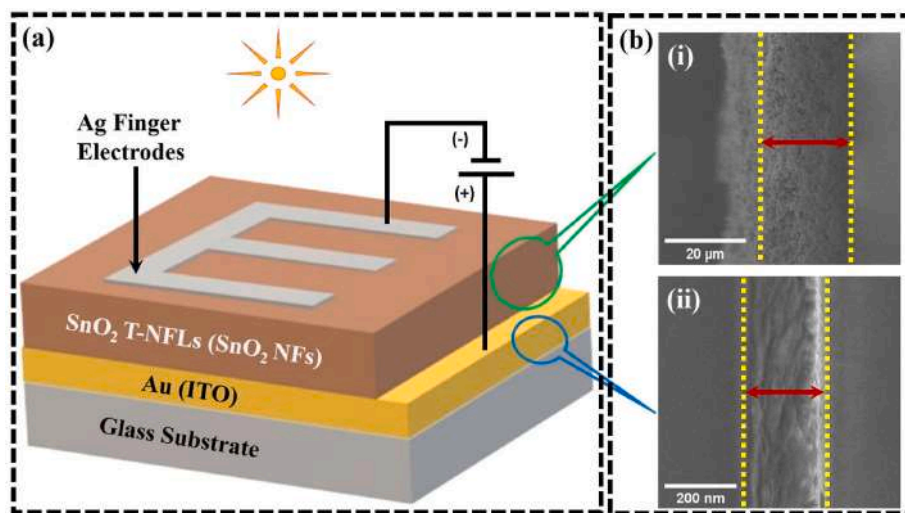


Fig. 4. (a) Schematic diagram of the fabricated devices under illumination showing the layer thicknesses. (b) The FESEM micrographs of cleaved devices indicating the thickness of (i) semiconductor and (ii) metal layers as 20 μm and 200 nm respectively.

Na_2SnO_3 is very poor in polar solvents, indicating hydrophobic nature. The hydrophobic-hydrophobic and hydrophilic-hydrophilic interactions may have confined crystal growth in one direction and formed trichomes on the petals of the nano-flowers. However, more work is required to understand the growth dynamics. The chemical composition versus energy plots of the samples S_1 and S_2 under the EDS are shown in Fig. 1(d). Detailed analysis estimates the atomic ratio of Sn:O as 1:2 for S_1 and 1:2.5 for S_2 . The excess oxygen content of S_2 may have resulted from the absorption of atmospheric oxygen onto the surface of the complex hierarchical structure of T-NFLs. The crystal structures of the samples were investigated using XRD, and the diffraction patterns are shown in Fig. 2. The crystallographic planes are labelled and compared with JCPDS file # 00-041-1445. The x-ray diffraction lines are attributed to the tetragonal rutile structure [32] of the samples. From the prominent crystallographic plan (110), the lattice constants, c/a ratio, and unit cell volumes have been calculated and are summarized in Table S11 (see SI). Notably, the lattice parameters (a , b , and unit cell volume) decrease in the order bulk $> S_2 > S_1$. This may be due to oxygen vacancies (OVs) mediated local lattice disorders [33]. Further, the diffraction peak positions and line widths of the samples S_1 and S_2 are observed to be shifted and broadened, indicating the presence of the size effect and vacancy dominated tensile stress and compressive stress in the samples [34,35]. Using the Debye-Scherrer Method (DSM), Williamson-Hall Method (WHM), and Size Strain Plot Method (SSPM) [36,37], the crystallite size, stress, strain, and surface free energy of the samples were estimated and listed in Table S12 (see SI). From SSPM, it has been observed that the lattice strain and free energy of sample S_1 are greater than S_2 . This may be due to the strong size confinement [38] in the NFs as compared to T-NFLs.

In order to understand the quantum confinement effect on the vibration modes, the samples were investigated using Raman spectroscopy and FTIR measurements. The results are shown in Fig. 3 (a, & b-c). As observed from Fig. 3 (a), the Raman peaks appearing at 168.443 cm^{-1} , 461.449 cm^{-1} , and 632.173 cm^{-1} refer to the B_{1g} , E_g , and A_{1g} Raman modes of S_1 respectively, indicating different degrees of stretching modes of Sn-O bonds [39]. Similar stretching modes are also observed in sample S_2 at 166.385 cm^{-1} , 448.455 cm^{-1} , and 623.639 cm^{-1} . The blue shift of Raman Peaks in S_1 compared to S_2 is possibly due to the presence of excess structural strain [40] (as obtained from SSPM) and/or a low concentration of defects [41] in S_1 . Again, as shown in the inset of Fig. 3 (a), the infra-red (IR) active Raman peaks, E_u TO (Transverse Optical), A_{2u} TO, and A_{2u} LO (Longitudinal Optical), appeared at 234.452 cm^{-1} , 523.276 cm^{-1} , 690.609 cm^{-1} for S_1 and 233.452 cm^{-1} , 506.021 cm^{-1} ,

679.204 cm^{-1} for S_2 respectively. The appearance of the IR-active modes may be due to the structural modifications induced by the size confinement effect [42] and the presence of disorders like oxygen vacancies (OVs) in the material [43] and lattice strain [44]. Apart from the above six peaks, additional peaks α , β and γ are observed at 139.573 cm^{-1} , 209.469 cm^{-1} , 594.030 cm^{-1} for S_1 and 138.022 cm^{-1} , 166.385 cm^{-1} , 584.016 cm^{-1} for S_2 respectively. The origin of peak α , may be due to the corner zone mode arising mainly from the wrinkle effect [45]. Similarly, the appearance of peaks, β and γ are due to the presence of SnO_x type materials with variable oxidation states of Sn [46] and defects in the structures, mainly oxygen vacancies (OVs) [45] respectively. In order to trace the IR vibrations, the experimental FTIR data were deconvoluted using the Gaussian function and plotted as Fig. 3(b and c). The low energy vibrational bands mainly correspond to O-Sn-O or Sn-O-Sn vibrational stretching (lattice vibrations) [47]. The peaks e_1 (516.784 cm^{-1}) and e_2 (507.714 cm^{-1}) correspond to the terminal oxygen vibrations [48] arising from the stretching of Sn-O bonds [49]. The quantum confinement induced characteristic FTIR peaks g_1 and g_2 have been observed at 575.332 cm^{-1} and 557.823 cm^{-1} respectively [50]. The IR active modes A_{2u} TO, $3E_u$ TO and A_{2u} LO have peaked at 534.953 cm^{-1} (f_1), 646.460 cm^{-1} (h_1), 724.383 cm^{-1} (j_1) for S_1 and at 523.191 cm^{-1} (f_2), 612.706 cm^{-1} (h_2), 703.099 cm^{-1} (j_2) for S_2 respectively [50]. The peaks i_1 at 690.629 cm^{-1} and i_2 at 664.848 cm^{-1} are due to the symmetric stretching of the Sn-O-Sn bond [51]. The shifting of FTIR peaks towards high energy values in S_1 as compared to S_2 may have resulted from the size effect [52], indicating the smaller size of NFs as compared to T-NFLs [52].

The optical absorption and emission spectra of S_1 and S_2 are shown in Fig. 3(d) and (e) respectively. From the excitonic peak bound absorption spectra, the band gaps of the samples S_1 and S_2 are found to be 3.74 eV and 3.73 eV respectively, as compared to the bulk band gap of 3.60 eV [19]. This reveals the size dependent widening of the band gap as commonly observed in nano-scale materials [53]. Again, the band gap of S_2 is redshifted from S_1 , which may be arising due to the confinement effects [53] from the amalgamated nano-flake and nano-rod structures of T-NFLs. The emission spectra shown in Fig. 3(d) and (e) exhibit luminescence, appearing at Gaussian fitted peaks p_1 , q_1 , r_1 , s_1 , t_1 , u_1 , v_1 at 2.70 eV, 2.82 eV, 2.93 eV, 3.06 eV, 3.21 eV, 3.28 eV, 3.42 eV for sample S_1 and peaks p_2 , q_2 , r_2 , s_2 , t_2 , u_2 , v_2 at 2.69 eV, 2.82 eV, 2.93 eV, 3.04 eV, 3.17 eV, 3.28 eV, 3.43 eV for sample S_2 . In comparison with the estimated band gap from absorption studies, the luminescence lines appearing at 3.42 eV (v_1) and 3.43 eV (v_2) refer to the radiative $E_{CB} \rightarrow E_{VB}$ (E_{CB} is the conduction band minima and E_{VB} is the valence band

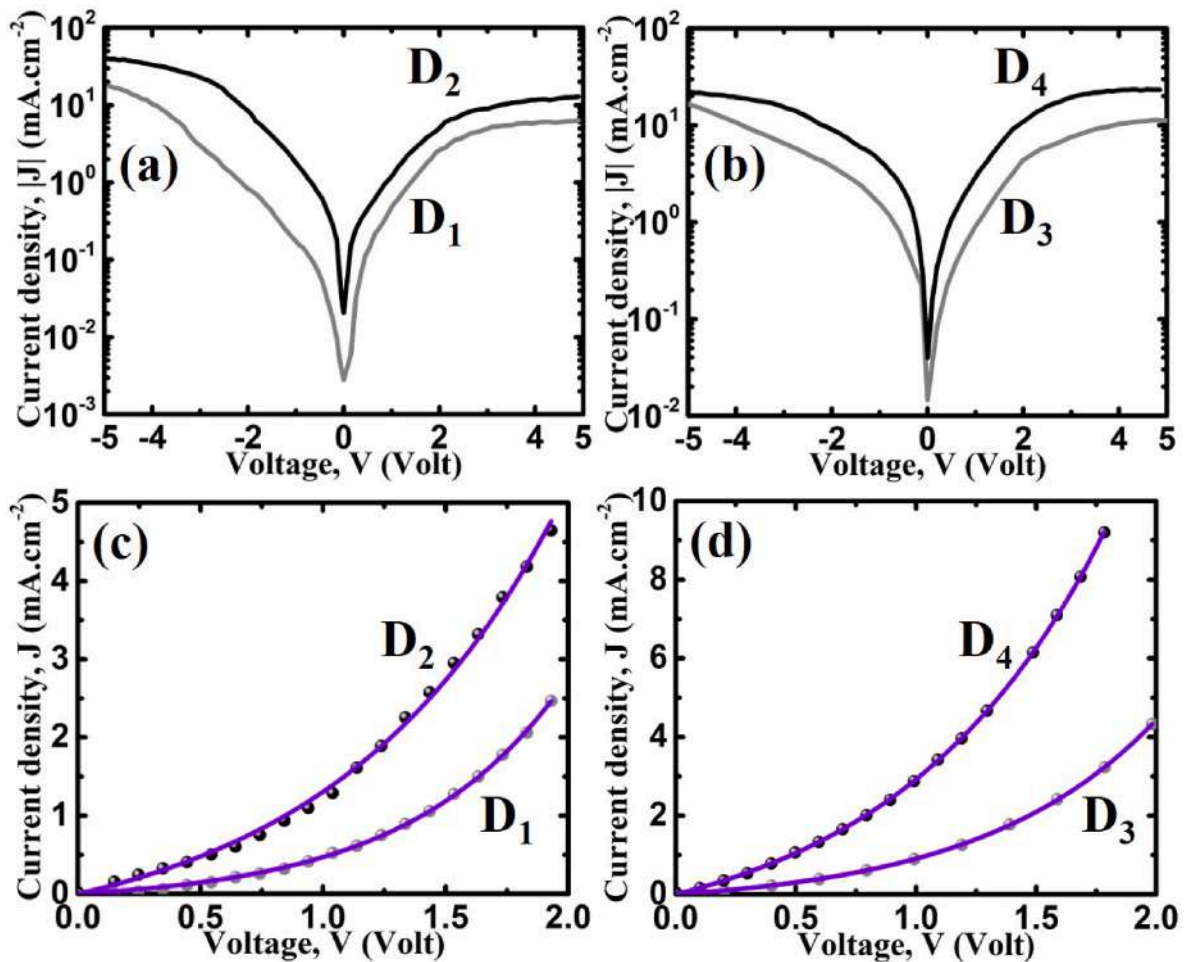


Fig. 5. $\log(J)$ – $\ln(V)$ curves of (a) D₁ (grey solid line) and D₂ (black solid line), and (b) D₃ (grey solid line) and D₄ (black solid line). (c) and (d) are the forward bias characteristics of D₁ (grey spheres), D₂ (black spheres), and D₃ (grey spheres), D₄ (black spheres) respectively, with fitted curves (violet solid line) using the TE model.

maxima) transition of electrons from the conduction Sn 4p to the valence O 2p band [54]. Further, in case of TCO, the multivalence nature of Sn introduces various intrinsic defect levels within the band gap with fast radiative transitions [55]. The major defect levels originate from interstitial- and vacant- Sn sites and interstitial- and vacant- O sites [55]. Moreover, according to Kilic and Zunger [55] et al., and Fang et al. [56], interstitial Sn²⁺ dominated transitions yield red emission. In our samples, the absence of luminescence at the same level rules out the involvement of Sn interstitial defects mediated transitions. Nevertheless, the origin of the remaining PL peaks can be assigned to the following transitions. In common TCO, there are three types of oxygen vacancies (V_O), viz., neutral oxygen vacancy (V_O^0), singly positively charged oxygen vacancy (V_O^+), and doubly positively charged oxygen vacancy (V_O^{++}) [57]. Notably, at ambient temperature, the dissociation of some V_O^0 gives rise to V_O^+ states and conduction electrons. Now, the V_O^+ state interacts in two possible ways, viz, (i) bound to the nearest Sn⁴⁺ to form a V_O^+ donor level below the conduction band, and (ii) accept a hole to form a V_O^{++} level above (around 1 eV [58]) the valence band. Interestingly, the V_O^{++} form a filled flat energy level above the valence band maxima called V_O^{++} acceptor level and a conduction band resonant empty level called donor level [57,58]. Therefore, the peaks p₁, q₁, r₁, s₁, (t₁ and u₁) and p₂, q₂, r₂, s₂, (t₂ and u₂) may have originated from the radiative transitions, $V_O^+ \rightarrow V_O^{++}$, $V_O^+ \rightarrow E_{VB}$, $V_O^0 \rightarrow V_O^{++}$, $E_{CB} \rightarrow V_O^{++}$ and $V_O^0 \rightarrow E_{VB}$ respectively. Here, the $V_O^0 \rightarrow E_{VB}$ is responsible for two emission peaks (t and u), implying a higher concentration of V_O^0 as compared to that of V_O^+ , and V_O^{++} in the

samples [59]. The Stoke's shift given by, $\epsilon_{ab} - \epsilon_{pl} = 2\delta\epsilon_{ph}$, where ϵ_{ab} is the maxima of the absorption band, ϵ_{pl} is the maxima of the band edge emission, ϵ_{ph} is the phonon energy (78 meV) [60], and δ is the electron-phonon coupling parameter [61]. Using the values of ϵ_{ab} , ϵ_{pl} , and ϵ_{ph} , the above equation yields the size dependent δ values of 2.09 and 1.94 for S₁ and S₂ respectively. This indicates, the electron-phonon coupling in S₂ has been relaxed due to the size hierarchical nano-trichome structure [62].

The electrical characteristics of the samples were evaluated by fabricating metal-semiconductor junctions comprising semiconductor samples with Au or ITO as the metallic part. The schematic diagram of the device structure is shown in Fig. 4 (a). Notably, the difference in work function between finger electrodes, Ag and samples prevails to be Ohmic contact. From a typical FESEM study of cleaved devices, as shown in Fig. 4 (b), the average thicknesses of the metal and sample layers were estimated as 200 nm and 20 μ m respectively. The semi-logarithmic current density-voltage (J-V) plots of the devices D₁ (grey line) and D₂ (black line) shown in Fig. 5(a) and D₃ (grey line) and D₄ (black line) shown in Fig. 5(b) exhibit the typical diode characteristics under dark condition. According to the literature, the work functions of n-type bulk SnO₂, Au, and ITO are \sim 4.5 eV, \sim 5.4, and \sim 5.2 eV respectively [63–65]. Therefore, the SBD characteristics observed in Fig. 5 are consistent with theory. In general, the Schottky behavior is characterized by the thermionic emission (TE) model; $J_D = J_0 \left[\exp\left(\frac{qV_D}{k_B T}\right) - 1 \right]$, where J_D is the current density through the junction, q is the electronic

Table 1
Junction parameters of the fabricated Schottky devices.

Device	J_0 (mA.cm ⁻²)	θ	Φ_B (eV)	χ (eV)
D ₁	0.140	2.42	0.86	4.52
D ₂	0.652	3.52	0.82	4.56
D ₃	0.302	2.83	0.84	4.36
D ₄	0.141	3.33	0.80	4.40

charge, V_D is the voltage across the junction, θ is the ideality factor, k_B is the Boltzmann constant, T is the absolute temperature, and J_0 is the reverse saturation current [66] where $J_0 = A^{**}T^2 \exp\left(-\frac{q\Phi_B}{k_B T}\right)$, with Φ_B as the barrier height, and A^{**} as the Richardson constant given by; $A^{**} = 4\pi q m^* k_B^2 / h^3$, consists of standard constants [67]. Considering effective mass, m^* as 0.3 m_0 (m_0 is the mass of electron), A^{**} value is 36.06 A cm⁻²K⁻² [67] for SnO₂. The J-V curves have been analyzed using the above TE model. The theoretical curves are shown by violet-colored lines in Fig. 5(c). From the best fit, the SBD junction parameters have been extracted and are listed in Table 1. Comparing devices D₁ and D₂, it has been seen that the barrier height of SnO₂ T-NFLs is less than NFs by 0.04 eV, with a difference in the ideality factor as 1.1. Notably, our studies affirm the temperature dependent increment in barrier height, which will be discussed elsewhere. Again, we know that $\Phi_B = \psi_m - \chi_{sc}$ where, ψ_m and χ_{sc} are metal work function and semiconductor electron affinity respectively [68]. Taking ψ_m^{Au} as 5.38 eV [64], the values of χ_{sc} for NFs and T-NFLs are found to be 4.52 eV and 4.56 eV respectively. Similar analysis has been followed for devices D₃ and D₄ that are shown in Fig. 5(d), and the barrier heights are estimated to be 0.84 eV and 0.80 eV respectively with difference in ideality factors by 0.50. Here, the varying barrier heights can be understood as follows. In general, the oxygen vacancies in MO introduce shallow defect layers within the band gap corresponding to V_O^0 , V_O^+ and V_O^{++} states. According to the literature, V_O^+ and V_O^{++} states are observed near the conduction band and valence band respectively [57,58]. Therefore, the increase in barrier height in sample S₁ over S₂ may be due to the dominance of V_O^{++} states. Considering the value of $\psi_m^{ITO} = 5.2$ eV [65], the χ_{sc} values for both the NFs and T-NFLs are found to be 4.36 eV and 4.40 eV respectively. Further, the barrier heights of devices D₃ and D₄ have lower values compared to D₁ and D₂ respectively. This may be due to the interaction of the metal part's electronic structure and work function with nano-scale semiconductors [69]. The high value of θ indicates rapid tunneling and recombination at the interface of S₂ based devices as compared to S₁ [70]. In comparison with recent reports by B. Jang et al. [68] and S. Jana et al. [71], our samples exhibit improved Schottky barrier height, which is an indicator of better rectification properties [72] (low forward voltage drop and low reverse leakage current). These characteristics

render it suitable for a diverse array of applications, encompassing high-speed switching as well as power conversion devices [73].

In order to explore the solar cell performance of the TCO based Schottky junctions, the devices were tested using a solar simulator under 1 sun light excitation. Here, the SBD junctions Au/SnO₂ and ITO/SnO₂ are forwardly biased (positive terminal connected to the bottom metal layer and negative terminal connected to the SnO₂ sample layer having Ohmic Ag finger electrodes) to evaluate the solar cell behavior of the devices. The presence of finger electrodes enables sufficient sunlight transmission through the active layer to reach the junction. Using energy-band diagrams, Fig. 6 schematically explains the origin of the solar energy conversion mechanism. Under forward bias, the electrons move from semiconductor to metal, ensuing the SBD J-V behavior. After photo-excitation, electron-hole pairs were formed across the band edges of the sample sides of the SBD junction. Due to the band bending and decrease in barrier height, the inbuilt electric field at the SBD junction efficiently separates the charge carriers and minimizes the rate of recombination augmenting the energy conversion [74,75]. The J-V characteristics of D₁ and D₂ are shown in Fig. 7(a) and (b) respectively, under illumination conditions. In order to ascertain the solar cell parameters, the data from the 4th quadrant were replotted as insets. From the analysis, the D₁ exhibits short circuit current density, J_{sc} and open circuit voltage, V_{oc} as 0.579 mA cm⁻² and 0.64 V respectively. Using power maximization protocol, the fill factor (FF) has been estimated to be 60% with solar cell efficiency (η) of 0.22%. Similarly, the J-V analysis of D₂, shown in Fig. 7(b), resulted the J_{sc} , V_{oc} , FF, and η values as 0.950 mA.cm⁻², 0.70 V, 61%, and 0.41%, respectively. Furthermore, the J-V curves of D₃ and D₄ shown in Fig. 8 were analyzed, and the parameters were found to be 1.228 mA cm⁻² and 2.003 mA cm⁻² for J_{sc} , 1.33 V and 1.56 V for V_{oc} , 52% and 57% for FF, 0.85% and 1.78% for η respectively. All of the solar cell parameter values for each device are listed in Table 2. The standard deviation in the devices' performance (conversion efficiency) assessed over several batches of samples is found to be 0.03. Again, according to the relation, $V_{oc} = \frac{k_B T}{q} \ln\left(\frac{J_{sc}}{J_0} + 1\right)$, where J_0 is the reverse saturation current, the V_{oc} is inversely proportional to J_0 [76]. Hence, the high V_{oc} value observed in our samples is an indicator of low reverse saturation current, implying very negligible recombination of the carriers at the interface [76]. Therefore, the high V_{oc} and excellent filling factor (>50%) observed in our samples suggests feasible power conversion applications [77,78].

4. Conclusion

In conclusion, the alkali ions (K⁺ and Na⁺) selective reduction and in-situ crystallization governed by hydrophilic and hydrophobic interactions in a hydrothermal growth yielded tailoring of SnO₂ size from

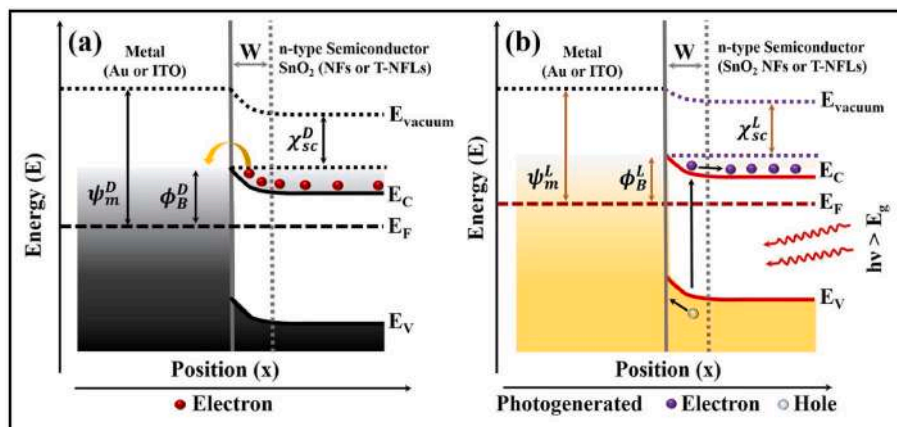


Fig. 6. Energy band diagrams of the devices under (a) dark and (b) 1 sun front illumination conditions.

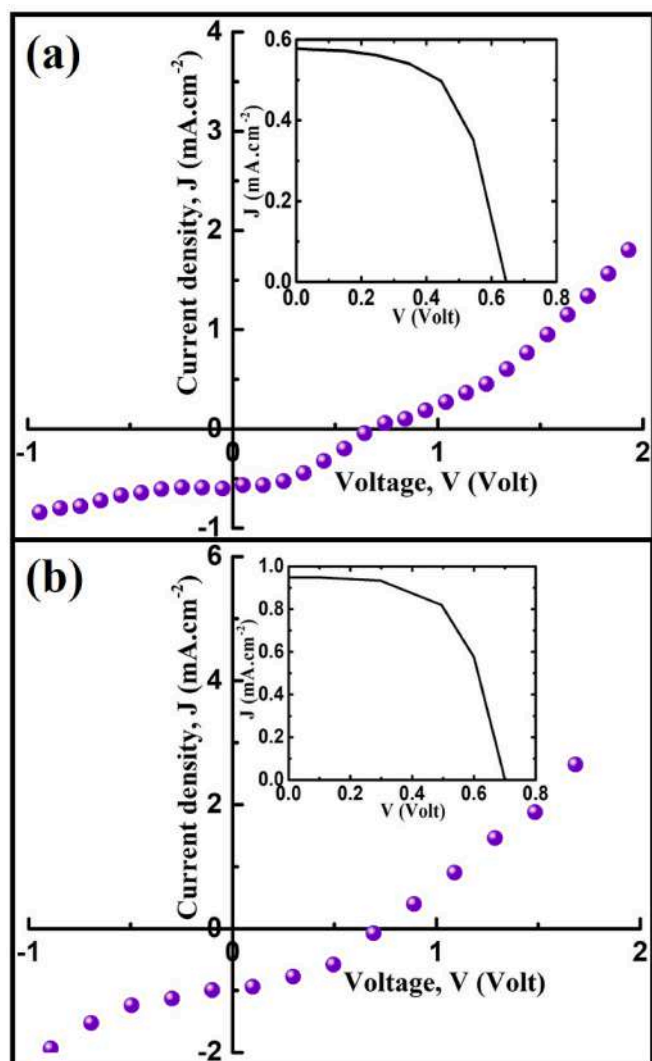


Fig. 7. $J \sim V$ characteristics of D_1 (a) and D_2 (b) under 1 sun illumination, with insets depicting the respective replotted fourth quadrant data.

nano-flakes to trichome nano-flowers. The photoluminescence analysis reveals oxygen defect ridden electronic transition accompanied by decrease in electron-phonon coupling parameter from NFs to T-NFLs. Through Schottky junction analysis, the electrical properties of the samples corroborate solar cell behavior with distinct reverse saturation currents. Compared to SnO_2 NFs, the T-NFLs have a higher photo-conversion efficiency ($1.76 \pm 0.03\%$) as well as a higher electron affinity (4.56 eV) and fill factor (61%). The observation of high open-circuit voltage reveals minimal recombination of the carriers at the interface due to its distinct structure. The aforementioned size hierarchical feature makes the SnO_2 nanomaterial suitable for prospective applications in Schottky junction based fast electronic devices and as active electron transport layers in solar cells.

CRediT authorship contribution statement

Gyanadeep Mallik: Writing – original draft, Methodology, Visualization, Conceptualization, Investigation, Data curation, Formal analysis. **Atanu Kabiraj:** Formal analysis. **Pragyan Paramira Dash:** Formal analysis. **Priyanka Kumari:** Formal analysis. **Utkalika Priyadarsini Sahoo:** Resources. **Pratap Kumar Sahoo:** Resources, manuscript review. **Satchidananda Rath:** Validation, Resources, Supervision, Conceptualization, Writing – review & editing, Funding acquisition.

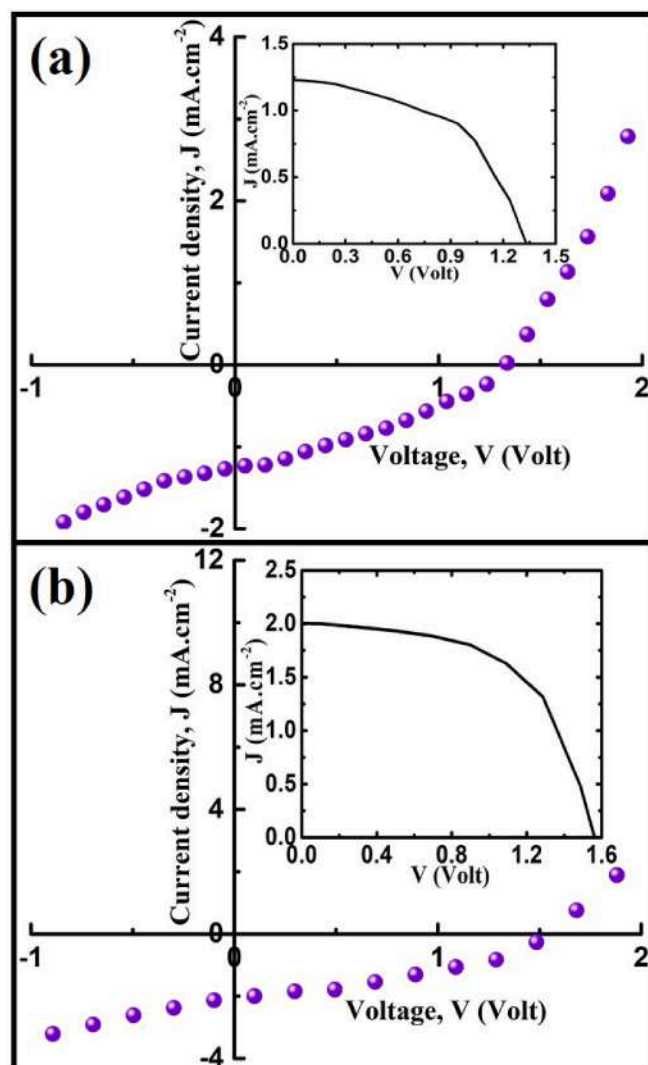


Fig. 8. $J \sim V$ characteristics of D_3 (a) and D_4 (b) under 1 sun illumination, with insets depicting the respective replotted fourth quadrant data.

Table 2

Solar cell parameters of the fabricated devices.

Device	J_{sc} ($\text{mA}\cdot\text{cm}^{-2}$)	V_{oc} (V)	P_{max} (mW)	FF (%)	η (%)
D_1	0.579	0.64	0.222	60	0.22
D_2	0.950	0.70	0.406	61	0.41
D_3	1.228	1.33	0.849	52	0.85
D_4	2.003	1.56	1.775	57	1.78

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

The authors acknowledge Nanomission, DST India scheme SR/NM/NS-68/2016 (G) for the financial support and the central

instrumentation facility (CIF) of IIT Bhubaneswar for the characterization of the samples.

Supplementary Information

The details of structural parameter analysis from the XRD data are available in supporting information.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.optmat.2023.114306>.

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