One pot synthesis of multi-functional tin oxide nanostructures for high efficiency dye-sensitized solar cells

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ABSTRACT

Photoanode plays a key role in dye sensitized solar cells (DSSCs) as a scaffold for dye molecules, transport medium for photogenerated electrons, and scatters light for improved absorption. Herein, tin oxide nanostructures unifying the above three characteristics were optimized by a hydrothermal process and used as photoanode in DSSCs. The optimized morphology is a combination of hollow porous nanoparticles of size $\sim$50 nm and micron sized spheres with BET surface area (up to 29 m^2/g) to allow large dye-loading and light scattering as well as high crystallinity to support efficient charge transport. The optimized morphology gave the highest photovoltaic conversion efficiency ($\sim$7.5%), so far achieved in DSSCs with high open circuit voltage ($\sim$700 mV) and short circuit current density ($\sim$21 mA/cm^2) employing conventional N3 dye and iodide/triiodide electrolyte. The best performing device achieved an incident photon to current conversion efficiency of $\sim$90%. The performance of the optimized tin oxide nanostructures was comparable to that of conventional titanium based DSSCs fabricated at similar conditions.

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1. Introduction

The photoanode or working electrode (WE) fabrication offers significant challenges in achieving high efficiency dye-sensitized solar cells (DSSCs). The WE is usually a mesoporous film of wide band gap metal oxide semiconductor (MOS) and has typically three functionalities: (i) to anchor large amount of dyes, (ii) to transport of photogenerated electrons to the collecting electrode (FTO), and (iii) to scatter the light additionally to improve the light absorption by the solar cells [1]. Mesoporous particles ($\sim$20–30 nm) of large surface area ($\geqslant$100 m^2/g) is required for loading large amount of dyes, [2,3] highly crystalline particles or wires with less defects are preferred for efficient transport, and larger particles ($\sim$200–300 nm) are required for light scattering [4–6].

Tin oxide (SnO_2) is a promising WE material in DSSCs owing to its wider band gap ($\sim$3.6 eV *vs.* $\sim$3.2 eV of TiO_2) and larger electron mobility (μ_n $\sim$100–250 cm^2 V^{-1} s^{-1}) than most frequently used TiO_2 (μ_n < 0.1 cm^2 V^{-1} s^{-1}) [7]. The wider band gap of SnO_2 improves device stability; whereas the UV absorption of TiO_2 degrades the dye and considerably reduce the operating hours of DSSCs [8]. The μ_n of SnO_2 is one of the highest in MOS, even in nanocrystalline form, in which form the μ_n sharply decreases by several orders of magnitude. The SnO_2 NPs have 50% higher μ_n

($\sim$3.63 × 10^{-3} cm^2 V^{-1} s^{-1}) than TiO_2 ($\sim$2.47 × 10^{-3} cm^2 V^{-1} s^{-1}) [9,10]. Order of magnitude higher μ_n is reported in SnO_2 nanowires and flowers than NPs [11]. Many wet-chemical methods are reported for synthesis of various morphologies of SnO_2 as WE in DSSCs; [12–15] but produced inferior efficiency (η). For instance, Wang et al. [16] synthesized hollow nanospheres (HNS) and reported η < 1% in pristine SnO_2. Liu et al. [17] fabricated coral-like porous SnO_2 HNS and developed DSSCs with $\eta \sim$ 1%. The η in the above studies remarkably increased several folds upon a $TiCl_4$ treatment. This enhancement is related to the increase in the Fermi energy of pristine SnO_2 upon $TiCl_4$ treatment, which otherwise occurs at lower energies than that of TiO_2 [18]. The lower Fermi energy of SnO_2 increase the energy loss at the SnO_2-dye interface and thereby impose a loss-in-potential at this interface and subsequently reduces the open circuit voltage (V_{OC}) and recombination resistance in DSSCs. Furthermore, SnO_2 has a low iso-electric point (pH $\sim$ 4–5) than that of TiO_2 (pH $\sim$ 6–7) so resulting in poor dye-loading [19–21] and consequently lower the short circuit current density (J_{SC}).

Herein, we optimized a hydrothermal process, with slight modifications in that used by Wang et al. [16] that developed a series of SnO_2 nanostructures. A temperature dependent growth process showed low crystallinity but high surface area for SnO_2 NPs synthesized at a low temperature ($\sim$150 °C) which gave inferior performance in DSSCs as is conventionally observed. Increase in temperature ($\sim$180 °C) lead growth of HNS ($\sim$700–800 nm) along

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with small NPs. The particles synthesized at a higher temperature $\sim$200 °C showed an optimum mixture of SnO_2 NPs and HNS with improved crystallinity, desirable light scattering and transport properties. When these nanostructures were tested as a WE in DSSCs, the SnO_2 HNS synthesized at $\sim$200 °C showed best performance among the others with a highest η ($\sim$4.0%) achieved using pristine SnO_2 till date. The η was increased to $\sim$7.5% upon $TiCl_4$ treatment.

2. Experimental section

2.1. Synthesis of SnO_2 nanostructures

The materials were synthesized following Wang et al. [16] but with modifications. In our experiment, we reduce the concentration of the growth solution (16.5 mM) to nearly one half than that reported before (32.7 mM) [16]. In a typical procedure, $SnCl_2 \cdot 2H_2O$ (0.25 g) was added to a mixture of 1 N HCl (0.6 mL), ethanol (6 mL) and DI water (60 mL) ultrasonicated for 1 h. The resultant transparent solution was then transferred to an autoclave and kept at a pre-heated furnace at $\sim$150 °C for $\sim$24 h. After cooling to room temperature, the solution was centrifuged, washed three times with DI water and dried it at $\sim$60 °C in the oven for overnight. This sample was labelled as "sample A". The same procedure was applied for "sample B" and "sample C"; however, the furnace temperature was increased to $\sim$180 °C and $\sim$200 °C, respectively. The SnO_2 HNS were also synthesized using the reported procedure [16] to see its macroscopic particle distribution.

2.2. Characterizations

The annealed nanostructures were characterized for morphology, particulate properties, and crystal structure. Morphology and microstructure of the materials were studied by scanning electron microscopy (7800F, FESEM, JEOL, USA). The BET surface area of the materials were measured using gas adsorption studies employing Micromeritics (Tristar 3000, USA) instrument in the nitrogen atmosphere. High resolution lattice images and selected area diffraction (SAED) patterns were obtained using transmission electron microscope (TEM) operating at 300 kV (FEI, Titan 80–300 kV). Crystal structure of the material was studied by X-ray diffraction (XRD) technique using Rigaku Miniflex II X-ray diffractometer employing Cu Kα radiation (λ = 1.5406 Å).

2.3. SnO_2 paste preparation

Three hundred milligram of SnO_2 was dispersed in ethanol and added α-terpinol (18 wt.%) and ethyl cellulose (10 wt.%). The above solution was ultrasonicated for 1 h and heated up to $\sim$70 °C to evaporate ethanol until viscous slurry was formed.

2.4. Solar cell fabrications and testing

The FTO substrates were immersed in 0.1 M aqueous $TiCl_4$ solution at $\sim$80 °C for $\sim$40 min followed by annealing for $\sim$30 min at $\sim$450 °C and subsequently cooled to room temperature. The SnO_2 pastes was then coated using Doctor–Blade technique on the $TiCl_4$ treated FTO substrates (1.5 cm × 1 cm; sheet resistance $\sim$18 Ω sq^{-1}) and then heated at $\sim$450 °C for $\sim$30 min. Thickness of the sintered electrodes was studied by SEM. The thickness of the films was $\sim$8.5 μm and the active area of the cells was $\sim$0.12 cm^2. The sintered electrodes were further treated with aqueous $TiCl_4$ solution (0.2 M) for improving the connectivity between the grains as well as suppressing the electron recombination with the tri-iodide species in the electrolyte [22]. This post $TiCl_4$ treatments was done by dipping the electrodes in the solution at $\sim$70 °C for $\sim$30 min, washed it with DI water to remove the residual $TiCl_4$ and then sintered at $\sim$450 °C for $\sim$30 min. The sintered electrodes was then soaked in RuL_2 ($NCS)_2 \cdot 2H_2O$ (L = 2,2'-bipyridyl-4,4'-dicarboxylic acid (N3 dye, Solaronix) (0.3 mM) for $\sim$24 h at room temperature. The unanchored dye-molecules were removed by washing with ethanol. The DSSCs were sealed using a $\sim$25 μm spacer. A Pt-sputtered FTO glass was used as the counter electrode. The electrolyte was acetonitrile containing 0.1 M lithium iodide, 0.03 M iodine, 0.5 M 4-*tert*-butylpyridine and 0.6 M 1-propyl-2,3-dimethyl imidazolium iodide, which was injected through two small openings at the counter electrode.

Absorption and transmission spectra of the dye anchored electrodes as well as dye desorption test were recorded using a UV–vis NIR spectrometer (UV-2600 SHIMADZU, Japan). The current–voltage ($I–V$) characteristics of the assembled DSSCs were studied using a solar simulator (SOLAR LIGHT, Model 16-S 150) employing single port simulator with power supply (XPS 400) at AM1.5 conditions. The $I–V$ curves were obtained using a potentiostat (Autolab PGSTAT30, Eco Chemie B.V., The Netherlands) employing the NOVA® software. The level of standard irradiance (100 mW/cm^2) was set with a calibrated c-Si reference solar cell. To avoid stray-light effects, devices were properly masked to expose only the WE area. In DSSCs, two types of $I–V$ characteristics measurement are performed, the normal

scan mode where the voltage is changing stepwise from the short circuit ($V = 0$ or current = I_{SC}) to the open circuit ($V = V_{OC}$ or current = 0), and the reverse scan mode operate where the voltage sweep from open circuit state ($V = V_{OC}$) to the short circuit current state ($V = 0$). Usually reverse scan mode delivered better results than that of normal scan mode when the delay time is shorter than the time required for a cell to acquire its equilibrium state. This discrepancy between normal and reveres scan mode could be reduced by taking the delay time an order of magnitude longer than that required for the silicon based solar cells. During the $I–V$ measurement the delay time is necessary after each step of sweep voltage in order to stabilize the device. The most obvious characteristics of DSSCs $I–V$ measurement is the temporal response which is much low as compared to the silicon based solar cells. Therefore, sufficient time is required for DSSCs transit time from short circuit to open circuit [23,24]. In our experiment, the DSSCs were illuminated for 10 min under solar cells simulator at room temperature $\sim$25 °C to stabilize the temperature before measuring the $I–V$ curve. The applied bias voltage source was swept from short-circuit current (I_{SC}, at $V = 0$) to open circuit ($V = V_{OC}$, at $I_{SC} = 0$). Following are the $I–V$ measurement parameters: current range $\sim$0–1 mA, maximum time for open circuit potential determination $\sim$180 s, wait time $\sim$5 s, potential range $\sim$–0.200–0.900 V, step potential $\sim$0.00244 s, scan rate $\sim$0.02 V/s and delay time $\sim$0.122 s. Measurements were repeated for five times for each DSSCs.

The incident photon to current conversion efficiency (IPCE) measurements was done using the Bukoh Keiki (CEP-2000) instrument, Japan. Five sets of devices were fabricated using each SnO_2 nanostructures and the measurements were repeated for 10 times to assure the consistency in the values.

3. Results and discussions

3.1. Morphological properties

Fig. 1 shows the SEM images of the SnO_2 nanostructures synthesized at $\sim$150, $\sim$180, and $\sim$200 °C, respectively. They are labelled as samples A, B, and C, respectively. The SEM image of particles synthesized using the increased precursor concentration, as reported in the reference [16] (32.7 mM), is also shown in Fig. 1. More SEM images are shown in Supporting Information (SI) (Fig. S1, SI). Sample A consists of uniform particles of size $\sim$100 nm; a closer examination revels that the particles are aggregates of <10 nm sized grains. At $\sim$180 °C (sample B), a wider distribution of aggregates were observed with size up to $\sim$800 nm; however, basic building blocks of each particle were remained same ($\sim$10 nm). Bigger particles further grow >1 μm at 200 °C with relatively large size distribution (Sample C). On the other hand, the particles synthesized following the increased precursor concentration showed coarsening (Fig. 1d). Size distribution and properties of the aggregates were closely analyzed using TEM. Fig. 2a shows typical TEM images of the sample C. Spherical aggregates of large size distribution in the range of $\sim$50 nm–1 μm was observed; particles in each aggregate remain practically constant at $\sim$10 nm. All aggregates including the larger ones showed partial transparency to the electron beam; from which we infer that the aggregates are hollow. Hollow nature of the aggregates could also be observed from SEM (Fig. 1c). Crystallinity of the sample was judged from the high resolution transmission electron microscopic (HRTEM) lattice images and selected area electron diffraction (SAED) patterns, which are shown in Fig. 2b. More TEM and HRTEM images are presented in SI (Fig. S2, SI). The HRTEM images showed aggregates of defect free nanograins and SAED pattern showed diffraction spots oriented along a circle. These observations show that the particles are of high crystallinity. In the X-ray diffraction (XRD) pattern, sharp and intense peaks of the sample C reveal that they are highly crystalline as observed from the HRTEM images and SAED patterns. Smaller particles with superior crystallinity are recommended for efficient charge transport in DSSCs while anchoring large amount of dyes [25]. The specific surface area, pore size and volume distribution were studied by Brunauer–Emmett–Teller (BET) method in nitrogen adsorption and desorption environment. The particulate properties of the samples from the above study, such as surface area, pore size and volume distributions are listed in Table 1. The BET surface area were $\sim$50, $\sim$45, and $\sim$29 m^2 g^{-1}, respectively for samples A, B, and C. The