Influence of tungsten on electrical properties of TiO_2 Nanowires in Hybrid Solar Cells

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Abstract

This study was done on the rectangular bunched TiO_2 nanowires (NWs) and W doped TiO_2 nanowires (NWs) which were grown on FTO substrate by hydrothermal method. A Scanning Electron Microscopy (SEM) was used to obtain the structural changes and morphologies. The hybrid nanostructure devices consisted of FTO/ grown nanowires/SQ2/P3HT/Ag layers. The hybrid nanostructured device performances were analyzed by current density–voltage (J(V)) measurement. An absolute energy conversion efficiency of 1.83% has been demonstrated under 100mWcm^{-2}. Noticeably, J_{SC} was improved with W incorporating in TiO_2 nanowires which enhanced the power conversion efficiency (η).

Key words: hydrothermal method, nanowires, SEM, J–V characteristic

Introduction

One of the main challenges of our society is the growing demand for energy. Not only is the world's population growing rapidly, but also the energy consumption is increasing due to more and more nations becoming industrialized. Approximately 30% of the world population still remain with insufficient electricity. The biggest fraction of the world's power supply relies on burning fossil carbon sources, leading to the emission of the greenhouse gas CO_2. The effect of atmospheric CO_2 on global warming is obvious and there is the rapidly growing need for additional power. As a concept of clean energy, solar light harvesting is the use of photovoltaics, which directly convert incident solar light into electric energy. Solar power generation will certainly play an important role in low greenhouse gas future. Today, the photovoltaic industry is almost completely dominated by solar cells based on Si.

Si photovoltaics exhibit high power conversion efficiencies (PCEs) in the order of 30% for research solar cells and can be operated for several years. However, although Si is the most abundant element on earth, it almost never occurs as a free element but rather as oxide SiO_2. Extraction of elementary Si is highly energy consuming and only high–purity and nicely crystalline Si is suited for high performance photovoltaics. Accordingly, fabrication of Si solar cells is expensive. New photovoltaics requiring less energy intensive and less costly fabrication processes are desirable. Low temperature processed solar cells have emerged as promising candidate in the photovoltaic industry for large–scale commercial production. The new generation solar cells are commonly

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based on metaloxide with different devices architectures. Hybrid solar cells are motivated by the idea to combine advantages of both photoactive organic and inorganic semiconductors to form a type 2 heterojunction. The most commonly used materials in hybrid solar cells are ZnO, TiO_2, SnO_2 and CdSe as electron transporting layer, combining with dye, quantum dots as light sensitizer, P3HT, PCPDTBT and spiro–OMeTAD as hole selective materials instead of liquid electrolyte. Nanostructured titanium dioxide (TiO_2) is one of the most fascinating materials in new generation solar cells, superconductor and water treatment because of its abundance, high chemical stability, low cost and non–toxic nature. TiO_2 is also used as electron transport layer. A lot of investigations have been attempted in the hybrid device structure including several architectures and various combination of inorganic/organic materials.

Oxide nanowire arrays are studied for their applications to solar cells. It is demonstrated that the nanowires can provide direct pathways for electron transport in dye–sensitized solar cells and therefore, while forming photoelectrode films, they offer better suppression of charge recombination than nanoparticles. Samples for the present study are synthesized in the form of nanowires by hydrothermal method.

Experimental Methods

Hydrothermal Growth

Fabricated hybrid solar cells in this work consist of a FTO/TiO_2(NWs)/SQ2/P3HT/Ag or FTO/W:TiO_2(NWs)/SQ2/P3HT/Ag structure. Initially, fluorine–doped tin oxide (FTO)–coated glass (Solaronix, 15Ω/sq) were cut into pieces of approximately 1.4×1.4 cm^2. Then, the FTO substrates were cleaned with acetone and isopropanol for 10min each in an ultrasonic bath. Subsequently, the samples were dried with nitrogen. Both TiO_2 and W–doped TiO_2 were synthesized by using the hydrothermal method. 15ml of deionized water, 15ml of hydrochloric acid (37 wt %)(Sigma–Aldrich), and 525µl of titanium tert–butoxide (Sigma–Aldrich, >99%) were mixed in an autoclave and stirred continuously for 15 min. For nanowire growth, the cleaned FTO coated glasses were placed into the autoclave for the hydrothermal process at 180°C for 3h. After being cooled to room temperature, the resulting samples were rinsed with DI water and then dried with nitrogen.Then the substrates were heated in air at 500°C for 30 min.W doping was achieved through the addition of 10mg of tungsten hexachloride (Sigma Aldrich, 99.9%) dissolved in 10ml of DI water and 10ml of concentrated HCl at 180˚C for 1h, with volumes between 100 to 300µl for various dopant concentrations in solution. The W precursor was added directly to the growth solution, after the Ti precursor, using the same reaction conditions as previously described.

Solar Cell Fabrication

Solar cell fabrication was proceeded by decorating the nanowire surface with a squaraine dye (SQ2) (Mitsubishi Chemicals) monolayer using a 0.2mM dye bath in ethanol for 3h. The samples were then rinsed with isopropanol to remove unanchored dye and dried under nitrogen gas. Before spin coating P3HT (Rieke Metals, 69kDa) (40mg/ml dissolved in chlorobenzene) at 1500rpm for 110s, the samples were pre–wetted in chlorobenzene. Subsequent post–annealing was done at 120°C for 5min in order to remove excess solvent. After the spin–coating of the hole transporter, P3HT, from a chlorobenzene solution, the devices were deposited a 130nm thick of silver through thermal evaporation at 10^{-6} mbar. All processes were performed under ambient condition.

Device Characterization

Scanning electron microscopy (SEM) images of nanowires were taken on a Zeiss Crossbeam 1540 SEM at 12keV accelerating voltage to characterize the surface morphology and structural properties. The samples were electrically contacted to stubs by either carbon tape or silver paste. The current density–voltage (J(V)) and external quantum efficiency (EQE) measurements were acquired by a Keithley 2400 source meter and controlled with a self–written LabVIEW program. The devices were recorded under simulated solar light using a LOT–Oriel LS0106 solar simulator with an AM 1.5G solar spectrum and a light intensity of 100 $mW.cm^{-2}$. Cells were illuminated through a shadow mask with a resulting active area of 0.125 cm^2.

Results and Discussion

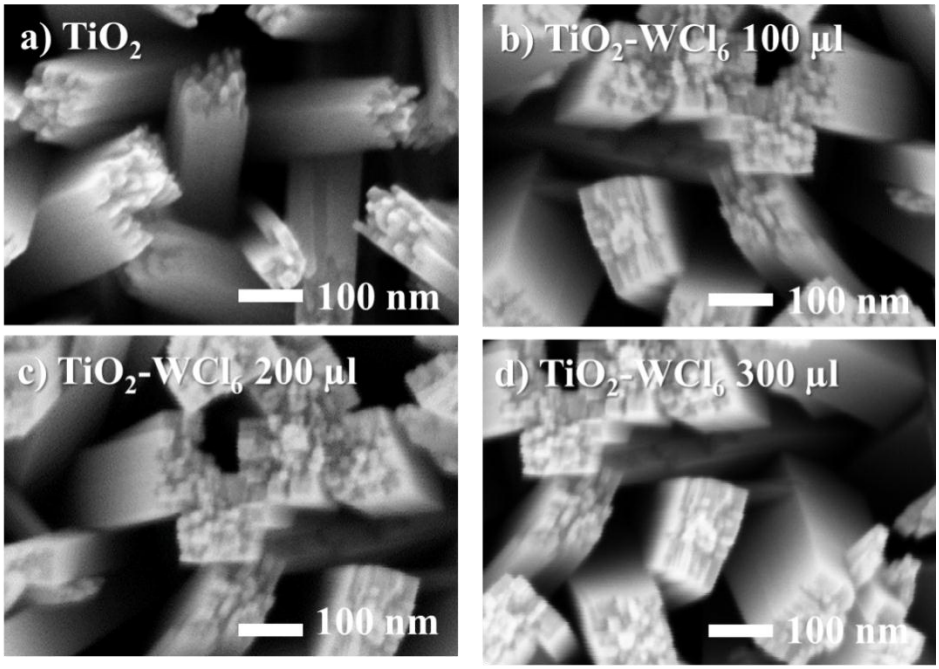

Figure 1 |(a) SEM image of TiO_2 NWs (b) SEM image of TiO_2NWs with 100µl of W doping (c) SEM image of TiO_2NWs with 200µl of W doping (d) SEM image of TiO_2NWs with 300µl of W doping.

The present study deals with synthesis of tungsten doped TiO_2 (W:TiO_2) nanowires by hydrothermal method and evaluation of their performance in hybrid solar cells. Similarity in the ionic radii between W^{6+} and Ti^{4+} and availability of two free electrons per dopant are the rationale for the present study. Scanning electron microscopy (SEM) investigations of the surface morphologies of the undoped TiO_2 and W doped TiO_2 nanowire (NW) arrays are shown in Figure 1(a–d), respectively. A high density NW arrays of TiO_2 and W doped TiO_2 nanowire (NW) arrays are grown vertically on the substrate with diameters ranging from 100 to 300 nm and lengths of about 1000 nm. The square crystals shape nanowire arrays are achieved in which single NW arrays consist of several nanowires bundle together. Furthermore, there has slightly changes in structure, morphology, shape and size of the nanowires after W incorporation in the nanowires.

The results from the J–V measurements for the doped with different concentration and undoped devices are summarized in Table 1, specifically the characteristic J_{sc},V_{oc}, fill factor (FF) and power convention efficiency (η). Figure 2(a) shows the J–V curves with the parameters of J_{sc} = 5.96mAcm^{-2}, V_{oc}= 0.51V, FF = 0.43, and η = 1.27% of undoped TiO_2 device, J_{sc} = 7.14mAcm^{-2}, V_{oc} = 0.50 V, FF = 0.45, and η = 1.55% of the 100µl W:TiO_2 device, J_{sc} = 7.33mAcm^{-2}, V_{oc} = 0.51 V, FF = 0.43, and η = 1.54% of the 200µl W:TiO_2 device, J_{sc} = 7.20mAcm^{-2}, V_{oc} = 0.54 V, FF = 0.48, and η = 1.83% of the 300µl W:TiO_2 device under AM 1.5G illumination with an intensity of 100 mWcm^{-2}.

The plots show that the 300µlW:TiO_2 device has better performance on average with higher J_{sc}, V_{oc} and fill factor, resulting in increased η among these four solar cells. Upon W doping, J_{sc} increase strongly, which results in an improvement of power conversion efficiency by more than 30%. This increase in V_{OC} could be attributed mainly to the faster electron transport and lower recombination rates for the W doped device. As discussed above, this improvement in device performance cannot be attributed to any change in the organic layers but its nature is identical. In contrary to that, the electronic properties of the metal–oxide are noticeably changed. This substitution yields two free electrons that result in an improved conductivity since the effective carrier concentration is increased.

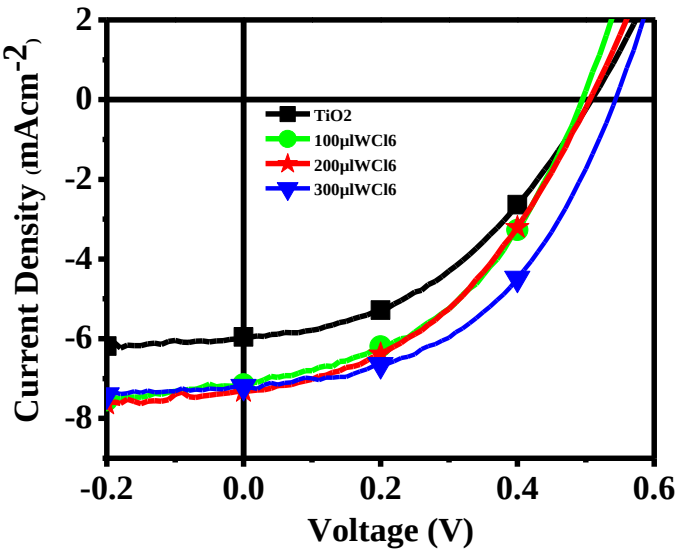

Figure 2 | J–V characteristics of hybrid solar cell using TiO_2 nanowires arrays with W doping and without doping (AM 1.5G, illumination 100mWcm^{-2}).

Table 1| Characteristic solar cell parameters recorded under simulated AM 1.5G solar illumination

Samples	V_{oc}(V)	J_{sc}(mA/cm^2)	FF	η (%)
TiO_2	0.51	5.96	0.43	1.27
100µlW:TiO_2	0.50	7.14	0.45	1.55
200µlW:TiO_2	0.51	7.33	0.43	1.54
300µlW:TiO_2	0.54	7.20	0.48	1.83

Conclusion

In this paper, W doped in metaloxide in hybrid solar cells is reported under working conditions. The improvement in the J_{SC} is attributed to an increase in charge density within the wires due to the W^{6+}dopant. Not only V_{OC} can be improved with W doping but also the fill–factor which enhances the power conversion efficiency,

indicating that the dopant plays a significant role in the charge transport of the nanowires.

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