Highly Efficient Dye-sensitized Solar Cells Based on Single Crystalline TiO_2 Nanorod Film

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Single crystalline anatase TiO_2 nanorods were successfully synthesized by surfactant-assisted hydrothermal method. A high light-to-electricity conversion yield of 7.06% was achieved by applying the TiO_2 nanorods as thin film of dye-sensitized solar cells.

Dye-sensitized solar cells (DSSC) based on mesoporous TiO_2 electrodes are currently attracting widespread academic and commercial intense investigation and interest for the conversion of sunlight into electricity because of their low-cost and environmentally friendly photovoltaics with good efficicencies comparable to that of silicon cell.[1] These cells consist of a mesoporous TiO_2 anode coated with a monolayer of a sensitizing dye for light absorption and electron injection into the TiO_2 conduction band. A liquid electrolyte generally contains a redox couple I^-/I_3^- that serves as the redox medium to regenerate the dye molecules by reduction. In the cells, undoubtedly, the mesoporous titania films and the dyes are two of the key components for high-power conversion efficiencies. Research efforts have focused on improving this system by altering the particle size and morphology of TiO_2,[2] optimizing the fabrication and structure of TiO_2 film,[3–5] developing new sensitizers,[6] suppressing charge recombination[7] and improving interfacial energetic.[8] We also reported that high efficiency had been achieved with TiO_2 nanowires composed of many nanoparticles aligned with each other because of the "oriented attachment" growth, which implied that the electron transfer in TiO_2 film is an important parameter for DSSC.[9] Hence, we attempted to prepare nanorods in order to substitute "oriented-attaching" nanoparticles and estimate the performance of nanorod DSSC.

Experimental details were as follows: Firstly, cetyltrimethylammonium bromide (CTAB) is dissolved in distilled water at 308 K and the concentration was fixed at 0.05 M. After a transparent solution has been obtained, titanium isopropoxide (TIPT, 0.22 M) was added immediately into above CTAB solution with stirring under ethylenediamine (EDA) basic catalyst. White precipitation obtained by hydrolyzation of TIPT was then transferred into a Teflon autoclave, sealed with a stainless steel crust, and reacted at 433 K for 12 h. The resulting white solid products were centrifuged and washed with distilled water and ethanol. In the experiment, we found the diameter and length of nanorods can be controlled by mixing triblock copolymer of poly(ethylene oxide)$_{100}$–poly(propylene oxide)$_{65}$–poly(ethylene oxide)$_{100}$ (F127) with CTAB in the beginning, these results will be discussed in the following parts. The wet white precipitation is directly applied for the formation of film electrodes as reported in the references.[10] The morphology and features of the product were examined using XRD, TEM, and SEM. The *I–V* characteristics were measured using an AM 1.5 solar simulator (100 mW/cm^2 Bunkoh-Keiki co., Ltd., CEP-2000). The cell size was 0.25 cm^2. The composition of electrolyte is 0.1 M of LiI, 0.6 M of 1,2-dimethyl-3-*n*-propylimidazolium iodide (DMPII), 0.05 M of I_2, and 0.5 M of 4-*tert*-butylpyridine (TBP) in methoxyacetonitride.

Figure 1A showed the TEM image of nanorods prepared in CTAB. Long rods with the diameter 20–30 nm have been observed. However, it is not single and dispersed rods but branched or aggregated rods. When the copolymer F127, which is a strong adhesive on the surface of oxide, is added into the system, branched rod has been completely dispersed with almost the same diameter and the length of rod is drastically decreased (Figure 1B). Figure 1C shows the HRTEM image of an individual TiO_2 nanorod obtained in F127 and CTAB system. The clear lattice strips showed that the nanorods have high crystallinity with fewer defects such as microtwins, which is expected to be benefit for the transfer of electrons in the rods. The fringes of (101) planes with a lattice spacing of about 0.354 nm can be observed. The growth of nanorod is along the [001] direction. Figure 2 showed the XRD pattern of sphere TiO_2 and nanorods TiO_2 prepared in CTAB and (B) with and (A) without F127. The XRD pattern of the samples indicated that an increase in the relative (004)/(200) intensities has been observed, as a consequence of the extended crystalline domain along the *c* axis. From Figure 1A, it can be seen the rod with over 400 nm is longer than that in Figure 1B with 100–150 nm in length. However, the former gives the intensities ratio of (004)/(200) is only 0.84, which is smaller than 1 with short rods in Figure 1B. It hinted that the branched rods included a part of bulk titania, which can be observed in Figure 1A (arrow). After the addition of F127, the rods can be completely dispersed and independently grown into short rods without other shape, which is also the reason of control shape of nanocrystals with two or more ligands by wet chemical method.[11]

In order to evaluate the performance of cell composed of the titania nanorods (which is prepared with F127 except mentioned), a cell composed of titania particles P-25 was fabricated as a reference. The photocurrent–voltage characteristics of both cells were measured under same experimental conditions.

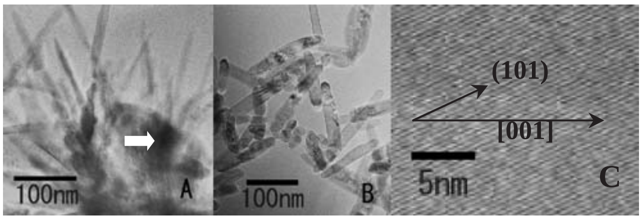

Figure 1. TEM image of nanorods prepared in CTAB (A) without and (B) with F127 and (C) HRTEM image of Figure 1B.

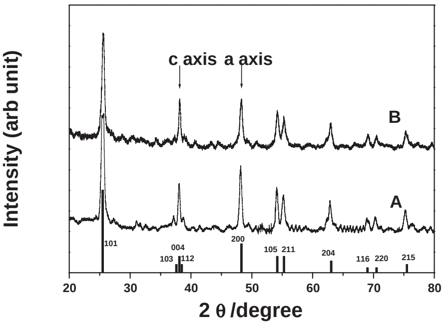

Figure 2. XRD pattern of nanorods prepared in CTAB (A) without and (B) with F127.

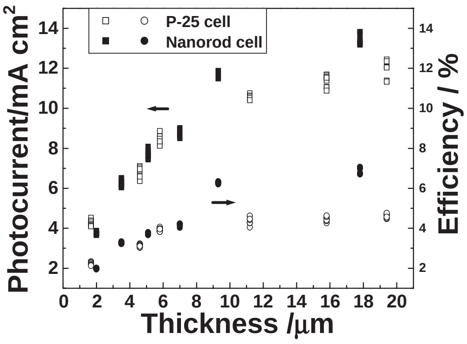

Figure 3. Dependence of photocurrent density and efficiency on the thickness of film in nanorod and P-25 cells.

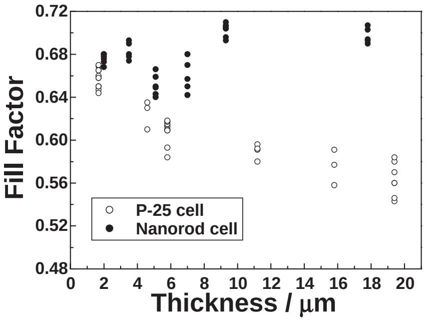

Figure 4. Fill factor of nanorod and P-25 cells.

Figure 3 shows the short circuit current density (J_{sc}) and efficiency obtained from the cells made of titania nanorods, together with those of P-25, against the film thickness. In the thin film region, the J_{sc} of the two cells was almost same, even P-25 cell has higher J_{sc}. However, the J_{sc} drastically increased in nanorods cell when the film thickness is over 8 μm. Similarly, the efficiency is gradually increased and not flat as in P-25 cell with thick film. We think that the high current density and efficiency might be attributed to the very high rate of electron transfer through the single crystalline TiO_2 nanorods, which is shown in Figure 1C by HRTEM. Comparing the nanoparticles, a nanorod or nanowire is constructed of isoelectronic materials that permit easy electron transport along the nanorod or nanowire.[12] Moreover, the use of a TiO_2 nanorods with high crystallinity instead of TiO_2 nanoparticles also contributes to the decreased number of contacts between titania materials, which make grain boundaries and act as electron traps. The fill factor of nanorod cells seems to confirm the guess, the result is shown in Figure 4. Fill factor represents the resistance of cell. When the electrons can be quickly and effectively transported without resistance, the value of fill factor is large, otherwise, the value will be decreased. The fill factor is decreased in P-25 cell with increasing thickness of film which indicated that the resistance is generally increased with semiconductive TiO_2 nanoparticles. However, the fill factor always is larger in nanorods cells although with thick film which hinted that the nanorod is an excellent candidate for the rapid transportation of electrons.”

A high conversion efficiency of light to electricity of 7.06% was obtained for the cell with TiO_2 single crystalline anatase nanorods. Short-circuit photocurrent density, open-circuit voltage, and fill factor were 13.4 mA/cm^2, 0.748 V, and 0.703, respectively. However, the P25 cell only give a highest efficiency of 5% (Supporting Information). It may be mentioned that the amount of dye adsorbed in the nanorod film is not drastically increased comparing the P-25 cell, which is expected to be mainly due to the large size of the nanorods with small surface area. Hence, the TiO_2 nanorod cell will be expected to adsorb more dye when the diameter of rods has been decreased into small size. Adding the rapid transportation of electrons, high efficiency of light to electricity will be achieved with small nanorod TiO_2 film. The work will be investigated in further work.

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