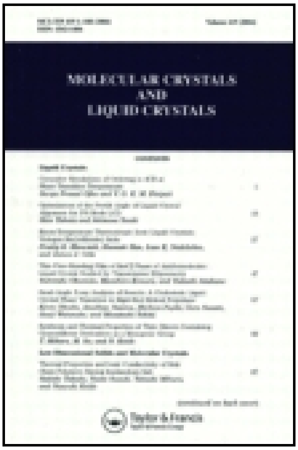

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Structure of TiO_2 Nanorods Formed with Double Surfactants

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Nanorod titania particles of anatase structure with 100 nm length and 20 nm width on an average were synthesized by a hydrothermal process with double surfactants system under relatively rigid tubular template in water. The rods have a tetragonal shape with washboard-like {101} surfaces, and covered properly with a Grätzel dye, exhibiting a high efficiency of light–to-electricity.

Keywords: double surfactants; microscopy; nanorod; solar cell; titania

INTRODUCTION

Development of renewable energy resources is an urgent issue in the near future. One fascinating strategy for the renewable energy is the development of dye-sensitized solar cells (DSSCs); they are extremely promising since they are made of low-cost materials and do not inquire elaborate apparatuses to manufacture. At present, the cell system has already reached conversion efficiency exceeding 11% [1,2]. Nevertheless, the energy conversion efficiency has not yet reached a level for commercial devices that can actualize lower cost than that of conventional electricity generation. Further technological improvement is needed for DSSCs. Since titania is the most capable material for the electrode of DSSCs, particularly titania small granular particles have

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been synthesized so as to fabricate porous network film as the electrode material in many cases, aiming at higher conversion efficiency attributable to larger amount of dye adsorbed on such nano-structured system. As known well, there should be many factors to control the efficiency; that is, particle size, particle morphology, calcination temperature, film quality, interface between titania and dye as well as electrolyte composition and material, sensitizing dye, and so on. Among them, control of particle morphology and structure are insisted in improving and optimizing carrier generation and transport, and in formation of appropriate interface with dyes. Along this guideline, many attempts have been done especially in formation of nano-scaled small particles. However, not only the size control of titania but also its shape and surface control could contribute on many issues in relation to improvement of efficiency of DSSCs; charge transport and carrier injection at interface. From this view, we have synthesized various shapes in nanometer scale in addition to nanoparticles [3]; nanorods [4], nanowires [5] and nanosheets [6] as summarized together with other previous reports in a review [7].

In the present study, we focus mainly on morphology and structure of TiO_2 nanorods which are especially effective to improve transportation of carriers in electrode by avoiding carrier traps occurring in the case of granular films. Electron microscopic analysis of the nanorod devices was carried out, and discussed on the shape formation process and interfaces of dye adsorbed.

EXPERIMENTAL

The nanorods have been synthesized from hydrolyzation of titanium isopropoxide under ethylenediamine basic catalyst by hydrothermal process (433 K, 6–12 hrs) using 10 wt% of blockcoploymer (F127; poly(ethyleneoxide)$_{100}$-poly(propyleneoxide)$_{65}$-polyethyleneoxide)$_{100}$) and 0.05 M of a surfactant of cetyltrimethylammonium bromide (CTAB) as a double surfactants system reported already [4,8]. Following the reported method, we prepared the nanorod sample with lengths of about 100 nm and diameters of about 20 nm after hydrolyzation. Such rod shape is stable in DSSC device even after high temperature calcination at 770 K. It should be noted here that rod-shape titania can be also synthesized with a single surfactant of CTAB, but the rods could not keep their shape during the high temperature calcination, indicating that F127 is a key component to maintain the rod-shape. For structural examination, a transmission electron microscope (TEM) observation was performed with a JEOL-200CX operated at 200 kV and JEOL-4000EX equipped with a liquid helium stage

(Cryo-TEM) operated at 400 kV. The Cryo-TEM was adopted to observe the template structure in a water solvent before adding any other chemicals. Additionally 3D morphology was examined with a TEM of JEOL-2200FS with $\pm 65^\circ$ rotation sample stage.

RESULTS AND DISCUSSION

As shown in Figure 1(a), the synthesized TiO_2 has almost rod-shape. Figure 1(b) shows a typical high resolution image of the surface, where the sharp surface appears as a washboard-like, and the individual surface consists of {101} surface of anatase TiO_2. Electron diffraction patterns (not shown) indicated that the longer axis of nanorod is the [001] direction. The washboard {101} surfaces are appropriate for accommodating the sensitizing dyes through carboxyl groups of Grätzel dyes; for example, N719 dye of 1 $(Bu_4N)_4[Ru(dcbpy)_2(NCS)_2]$ [9], and furthermore the surface provides larger surface than simple flat surface rods. When the nanorods were observed on their dye adsorption, actually the {101} surfaces are uniformly covered with the dye (amorphous-like contrast on the surface) as shown in a high resolution TEM image of Figure 2. The thickness is about 1 nm that is nearly the same thickness observed in the case of nanoparticles. The high resolution TEM image shows clearly the regular atomic arrangement of anatase TiO_2, which means high crystallinity. Furthermore the 3D morphology of nanorods was examined by electron tomography with JEOL-2200FS to determine the whole shape of a nanorod. As a result (not shown here), the nanorod has a shape of tetragonal rod with the washboards on four surfaces parallel to the long direction (the c-axis) as schematically shown in Figure 2(b).

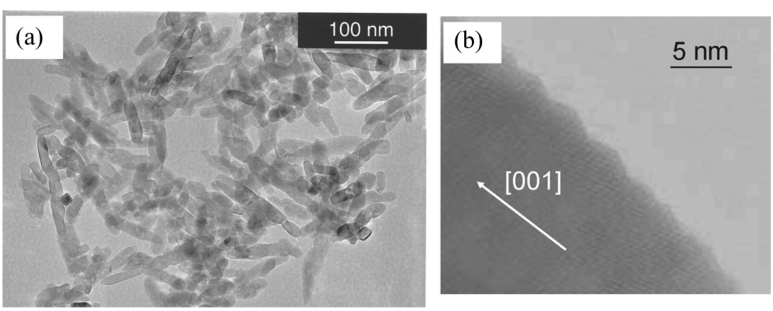
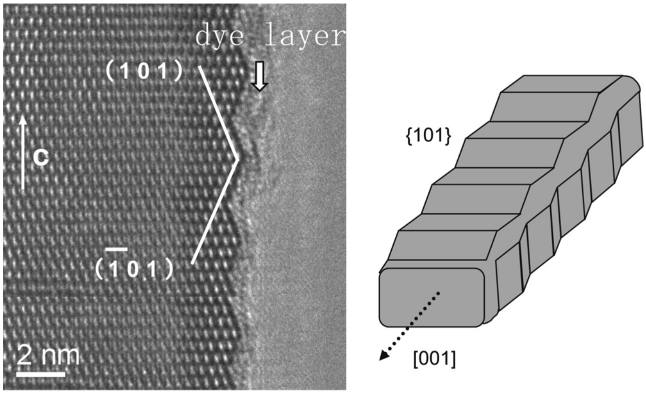


FIGURE 1 (a) TEM image of nanorods formed by the double surfactant process. (b) High resolution TEM image at surface.



(a) (b)

FIGURE 2 (a) High resolution TEM image at an edge of nanorod, where the surface is composed of {101} plane of anatase TiO_2 structure with washboard morphology. The surface is covered with N719 dye at the thickness of about 1 nm. (b) Whole shape of a nanorod with tetragonal shape.

An important scientific interest is why such nanorods are formed in the double surfactants method using F127 and CTAB. To get a hint on this point, we observed structures existing in the solution containing F127 or/and CTAB by Cryo-TEM. For the case of only CTAB, at the used concentration of 0.05 M CTAB, we could observe only a few faint specified contrast. Contrary to this, by using only F127 at 10 wt%, tubular micelle morphology was observed in Cryo-TEM image as shown in Figure 3, in which one can see a hexagonal packing of circular contrasts and a linear alignment of line contrasts, demonstrating various projections of a hexagonal tube alignment depending on relative electron beam incidences to the hexagonal alignment. The basic periodicity was estimated to be about 13.5 nm. As for the mixed template of F127 and CTAB, a typical Cryo-TEM image in Figure 4 shows also similar tubular morphology but of a basic periodicity of 11.7 nm, indicating slight shortening of the periodicity, comparing the case of only F127. The shortening of periodicity could be related to volume contraction and possibly to more rigid micelle formation. A relevant report has been published in a similar system [10], in which they used P123 (triblock copolymer similar to F127; EO_{20}-PO_{70}-EO_{20}) and CTAB to control mesoporous silicas by adjusting micellar properties. From measurements by X-ray diffraction, sorption isotherms and TEM, they have concluded that the micelle size is decreased by adding CTAB from that by single surfactant of P123, which is due to the fact that

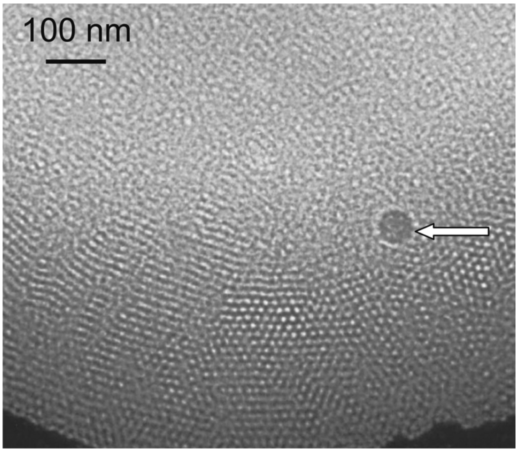


FIGURE 3 Cryo-TEM image of F127 water solution, where various contrasts are observed depending on the relative beam direction to a tubular hexagonal packing with a basic periodicity of about 13.5 nm. The white arrow in the figure indicates a small ice accidentally formed on the sample.

the existence of CTAB induces the hydration of hydrophobic PO block and decreases the volume of hydrophobic surfactant chain of P123. Following their hypothesis, the present double surfactant system with F127 and CTAB can be suggested to realize in the same way a compact and rigid tubular micellar structure that is especially advantageous to

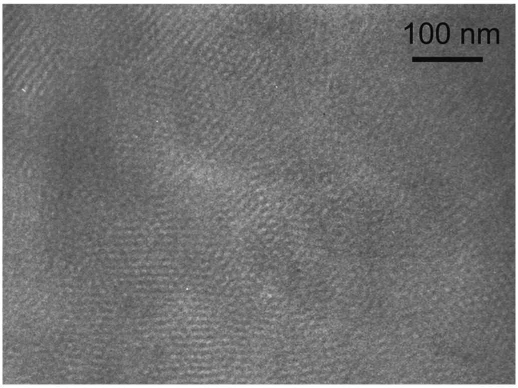


FIGURE 4 Cryo-TEM image of the double surfactants in water, showing also tubular morphology as F127 solution, but the basic periodicity becomes shorter.

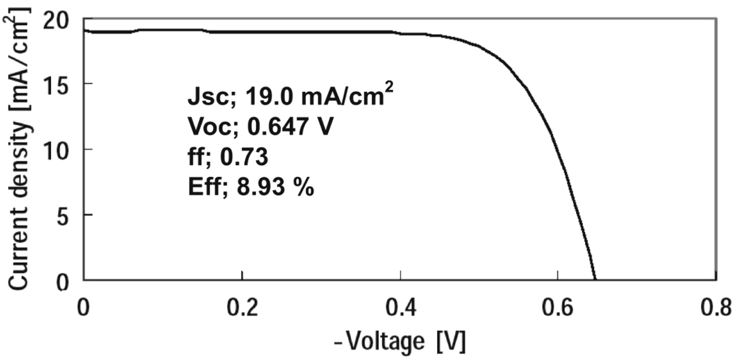


FIGURE 5 I-V curve measured for a nanorods DSSC formed with oleic acid additionally, whose efficiency is 8.93%.

form the high quality nanorods, even though the details of the formation process are still not clear.

As for the DSSC performance, in the case of widely used granular TiO_2 electrode, with increasing film thickness, the recombination of electrons is drastically increased owing to many connection barriers between the titania particles, and a saturation behavior of photocurrent is often observed at thick film cells. However, more slow saturation of photocurrent is characteristic in the naorods cell [4], indicating potential higher efficiency. In our previous reports [4], the efficiency of light–to-electricity was 7.34% when the photocurrent-voltage characteristics were measured with a cell size of $0.25\,cm^2$ using an AM 1.5 solar simulator under a electrolyte composition of 0.1 M LiI, 0.6 M 1,2-dimethyl-3-*n*-propylimidazolium iodide, 0.05 M I_2 and 0.5 M 4-*tert*-butylpyridine in methoxyacetonitrile. Recently the efficiency was improved up to 8.93% for the similar nanorods when used additional oleic acid as inhibitor on growth rate along a specified direction (Fig. 5).

In summary, we synthesized nanorod shape titania particles of anatase structure with 100 nm length and 20 nm width. The rods have a tetragonal rod with washboard-like {101} surfaces, and covered properly with the Grätzel dye of N719, realizing a high efficiency of light–to-electricity. The nanorods were synthesized by the hydrothermal process under double surfactants system, and are anticipated to be originated from the relatively rigid tubular template in water by using the double surfactants. Such shape control is one of the crucial objects to improve dye adsorption, transport and then efficiency of DSSCs. In future, the nanorods are useful to apply for multi-film layer, not a single component layer, to improve more the efficiency, because such fine tuning of TiO_2 layer structure is essentially important in device performance.

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