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The improvement of light scattering of dye-sensitized solar cells aided by a new dandelion-like TiO_2 nanostructures

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ABSTRACT

We present a new dandelion-like TiO_2 spheres by a modified hydrothermal method for manufacture of dye-sensitized solar cells (DSSCs). This construct is composed of numerous nanowires for employment as the scattering layer of DSSCs. Such morphology is produced by nucleation-growth-assembly mechanism. The size of the dandelion-like spheres and their morphology can be tailored by controlling the processing parameters of the modified hydrothermal process. TiO_2 nanoparticles with narrow size distribution are also synthesized by hydrothermal route for the active layer of DSSCs. The nanoparticles show pure anatase phase with average size of 40 nm, whereas the dandelion-like TiO_2 spheres are pure rutile structure with average diameter in the range 5–9 μm. A systematic study is performed in order to improve the photovoltaic performance of the DSSCs with different arrangement modes. First, the monolayer DSSCs with various thicknesses are prepared using pure nanoparticles. The highest power conversion efficiency (PCE) of 7.4% is obtained for the monolayer cell with thickness of 31 μm. Second, the double layer DSSCs containing an under-layer and an over-layer are reported. The double layer DSSC made of nanoparticles as the under-layer (with thickness around 31 μm) and mixtures of nanoparticles and dandelion-like spheres as the over-layer (as light scattering layer with thickness around 8 μm) shows the highest PCE of 8.3%. The improvement of cell efficiency is explained by triple function mechanism including significant increase in light scattering, dye sensitization and photo-generated charge carriers.

1. Introduction

Titanium dioxide (TiO_2), a semiconductor with three main alotropies including rutile, anatase and brookite, exhibits a wide range of potential technological applications such as photocatalysis of pollutants [1], gas sensors [2], energy-storage devices [3], self-cleaning coatings of windows and tile [4] and transparent conducting electrodes for dye-sensitized solar cells (DSSCs) [5]. In addition, not only it has numerous applications in industry, but also encompasses a great number of advantages same as being inexpensive and safe and compatibility with the body and environment.

The main stream of the research on DSSCs has been focused on development of materials which would enhance the conversion efficiency, simplify the production of the cell and assure their long-lifetime. In order to reach high conversion efficiencies, it is important to increase the electron injection and optical absorption. Since the electrode has huge surface area per projected area, solar cells made of dye-adsorbed nanoporous TiO_2 can drastically increase effective light absorption. Light scattering is already a well-known approach for boosting the optical absorption of photoelectrode in the conventional DSSCs [6]. In order to improve light scattering and dye loading simultaneously, double-layered films containing TiO_2 nanoparticles as the under-layer and TiO_2 nanowires [7], corn-like nanowires [8], nanospindles [9], nanotubes [10], nanofibers [11], nanorod-aggregates [12], hollow sphere particles [13] and multiwalled carbon nanotube–TiO_2 nanocomposite [14] as the over-layer has been proposed. Many efforts have been aimed to prepare TiO_2 nanostructures with various morphologies, including nanotubes [15], nanorods [16], three-dimensional (3D) hierarchical structures with hollow spheres [17], nanoflowers [18] and dandelion-like TiO_2 structure [19]. However, these morphologies have been employed for other applications rather than DSSCs. It seems that the dandelion-like rutile TiO_2 is an attractive morphology for the DSSC applications due to its facile electron transport and enhanced visible light scattering and absorption. On the other hand, rutile phase impresses an immense influence on scattering layer of DSSC due to its higher refractive index compare with the other phases of titania. Bai et al. [19] synthesized dandelion-like rutile TiO_2 structure containing several nanorods by the hydrothermal method using $TiCl_3$ as the main starting material as well as HCl, NaCl and NaOH. Such structure was employed for degradation of

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methyl orange under UV light illumination. Min et al. [20] reported dandelion-like rutile TiO_2 composed of numerous single-crystalline nanorods by a wet-chemical route using $TiCl_3$ as the starting material and LiCl. Such morphology showed good electrochemical properties.

We propose a concept of new dandelion-like TiO_2 nanostructure composed of numerous nanowires by a modified hydrothermal process. In addition, the morphology of the product can be tailored by controlling the processing parameters. The parameters are tailored in such a way that rice-like TiO_2 structure can also be produced. This construct is used as the scattering layer of a DSSC to improve the scattering effect and power conversion efficiency of the cell. The effect of arrangement modes of monolayer and double layer DSSCs composed of dandelion-like, rice-like and nanoparticles is investigated. Photovoltaic characteristics of double layer solar cells are also systematically studied compared with monolayer films made of pure TiO_2 nanoparticles.

2. Experimental

2.1. Preparation of anatase-TiO_2 nanoparticles

TiO_2 nanoparticles were prepared by the hydrothermal process using titanium tetraisopropoxide (TTIP) with a purity of 97% (Merck, Germany) as a titanium precursor, 2-propanol with purity of 99% (Merck, Germany) as a solvent. In the first step, TTIP was mixed with 2-propanol and stirred for 1 h at room temperature to obtain the molar ratio of $[H_2O]$:[TTIP]:[2-propanol] =0.055:0.013:0.258. During mixing, deionised water was slowly added to the solution in order to form TiO_2 sol. In the second step, the prepared sol was placed into 47 ml Teflon-lined stainless steel autoclave. The autoclave was heated at 180 °C for 12 h and subsequently cooled naturally to room temperature. The collected precipitates (i.e., anatase-TiO_2 nanoparticles) were washed with dilute ethanol several times and dried at 25 °C.

2.2. Preparation of dandelion-like TiO_2 nanostructures

Dandelion-like TiO_2 nanostructures were synthesized by hydrothermal process using $TiCl_4$, as the main precursor. $TiCl_4$ solution was prepared using $TiCl_4$ with purity of 99% (Merck, Germany), HCl with purity of 37% (Merck, Germany) and deionised water at room temperature. To control the pH, NaCl with purity of 99% (Merck, Germany) was added to the solution. The molar ratio of $TiCl_4$:H_2O:HCl:NaCl was 0.024:0.500:0.183:0.059. The solution was transferred into 47 ml Teflon-lined stainless steel autoclave. The autoclave was heated at 180 °C for 4 h and subsequently cooled naturally to room temperature. The collected precipitates (i.e., dandelion-like TiO_2 nanostructures) were washed with deionised water (five times) and with absolute ethanol (three times) and finally dried at 25 °C.

2.3. Preparation of rice-like TiO_2 nanostructures

Rice-like TiO_2 nanostructures were synthesized by the hydrothermal process similar to the previous procedure employed for synthesis of dandelion-like morphology. The only difference was that the autoclave was heated at lower temperature (i.e., 160 °C) for 4 h. The aspect ratio of prepared one-dimensional nanostructure was decreased with decreasing both reaction temperature and process time of the hydrothermal route. This can be explained by decreasing the reaction rate of growth species as a kinetics parameter. The collected precipitates (i.e., rice-like TiO_2 nanostructures) were washed with deionised water (five times) and with absolute ethanol (three times) and finally dried at 25 °C.

2.4. DSSCs assemblage

Different TiO_2 pastes with various morphologies and crystal structures were prepared using dandelion- and rice-like TiO_2 structures as well as TiO_2 nanoparticles. The pastes were prepared based on our previous work [21]. The photoanode electrodes in the forms of monolayer and double layer TiO_2 films were coated on fluorine doped tin oxide (FTO) substrate (7 Ω/sq) by a spin-coater (Modern Technology Development Institute, Iran).

Basically, two kinds of DSSCs in the form of monolayer and double layer films were fabricated in order to study the effect of different parameters on photovoltaic performance of the DSSCs. The monolayer DSSCs were consisted of two categories with different morphologies and crystal structures of TiO_2, (i.e., pure anatase-TiO_2 nanoparticles) for the first category and a mixture of TiO_2 nanoparticles and dandelion-like TiO_2 for the second category, as shown in Table 1. The effect of film's thickness on photovoltaic characteristics of DSSCs was studied for the first category cells in order to determine the optimal thickness. Furthermore, the effect of nanoparticle:dandelion-like weight percentage on photovoltaic characteristics of DSSCs was investigated for the second category cells in order to determine the optimal weight percentage.

Two categories of double layer DSSCs containing the under-layer, made of pure nanoparticles, and over-layers, composed of mixtures of 33.3 vol% dandelion- or rice-like nanostructures and 66.6 vol% nanoparticles, with almost the same thicknesses were also fabricated, as presented in Table 2. The over-layer played an absolutely integral role in light scattering, so it can perform as a scattering layer.

The deposited TiO_2 films were annealed at 400 °C for 2 h in air atmosphere for removal of utilized dispersing agent and binders in preparation of the paste. The post-treatment with $TiCl_4$ solution was applied to newly annealed TiO_2 electrodes as reported, previously [22]. An aqueous stock solution of 2 M $TiCl_4$ was diluted to 0.04 M. TiO_2 electrodes were immersed into this solution and stored in an oven at 70 °C for 30 min in a closed vessel. After

Table 1
Characteristics of TiO_2 monolayer solar cells.

Cell	Morphology	Crystal structure	Nanoparticle: dandelion-like (wt%)	Thickness (μm)
N8	Nanoparticles	Anatase	100:0	8.4
N11	Nanoparticles	Anatase	100:0	10.7
N13	Nanoparticles	Anatase	100:0	13.4
N20	Nanoparticles	Anatase	100:0	20.1
N27	Nanoparticles	Anatase	100:0	27.3
N31	Nanoparticles	Anatase	100:0	31.1
N37	Nanoparticles	Anatase	100:0	36.8
D	Dandelion-like	Rutile	0:100	31.1
ND31	Nanoparticles+dandelion-like	Anatase+rutile	75:25	30.6
ND11	Nanoparticles+dandelion-like	Anatase+rutile	50:50	31.2
ND13	Nanoparticles+dandelion-like	Anatase+rutile	25:75	31.9