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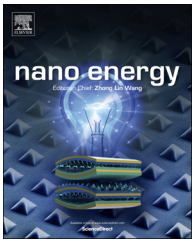

REVIEW

Soft processing of hierarchical oxide nanostructures for dye-sensitized solar cell applications

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Nanowire array

Abstract
To improve the performance of dye-sensitized solar cells (DSSCs), numerous hierarchically nanostructured anodes based on nanoparticle films and nanowire arrays have been constructed, exhibiting a high surface area for dye adsorption and the ability to scatter light. This review briefly summarizes the latest progress in conventional solution processing and soft processing routes for fabricating hierarchical TiO_2 and ZnO nanostructures on transparent conducting oxide (TCO) substrates for DSSC anodes. Soft processing routes, which directly fabricate functional materials with the desired composition, structure, shape, size, location, and orientation with low energy, have been demonstrated to be efficient methods for preparing hierarchical DSSC anodes based on nanowire arrays on TCO substrates.

Contents

Abbreviations: CBD, chemical bath deposition; DAP, diaminopropane; DSSC, dye-sensitized solar cell; ECD, electrochemical deposition; FTO, fluorine-doped tin oxide; HOMO, highest occupied molecular orbital; IMVS, intensity-modulated photovoltage spectroscopy; IMPS, intensity-modulated photocurrent spectroscopy; ITO, indium tin oxide; LbL-AR, layer-by-layer absorption and reaction; LUMO, lowest unoccupied molecular orbital; NC, nanocactus; ND, nanodendrite; NP, nanoparticle; NR, nanorod; NS, nanosheet; NT, nanotube; NW, nanowire; RT, Room temperature; TCO, transparent conducting oxide; TEM, Transmission electron microscopy; UV-vis, Ultraviolet-visible

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Introduction

Solar light is the most abundant renewable energy source and has great potential to meet future global energy demands. Photovoltaic conversion [1–4] and photocatalytic water splitting [5–10] are two promising techniques for efficient solar energy conversion to produce electricity and hydrogen, respectively. Photovoltaic solar cells, which directly convert solar energy to electrical power, have gone through three generations, from single-crystalline silicon solar cells [4], to thin-film semiconductor solar cells [4], to dye-sensitized solar cells (DSSCs) [4] and organic solar cells [4], to meet the long-term goal of low production and operating cost in addition to high-efficiency energy conversion for practical use. Although the conversion efficiency of organic solar cells has significantly increased [4,11], DSSCs are still better due to their higher efficiency, better stability, and longer lifetime [12].

Dye-sensitized solar sells

DSSCs, which combine nanotechnology and solar-energy technology, still attract great interests now since a breakthrough achieved by O'Regan and Gratzel in 1991 [13]. A typical DSSC is composed of a dye-sensitized high-surface-area TiO_2 nanoparticle (NP) film on a transparent conducting oxide (TCO) and a platinized counter electrode sandwiched together with an I^-/I_3^- redox electrolyte solution [1,14]. Solar radiation is absorbed by a monolayer of dye on the surface of the TiO_2 anode. Here we have illustrated the working principle of DSSCs in Figure 1. Electrons are transferred from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the dye, forming excitons. Exciton dissociation can only occur at the dye/TiO_2 interface. The electrons are then injected into the TiO_2 conduction band, which is just below the LUMO band of the dye. The electrons diffuse through the interconnecting network of the porous TiO_2 anode and are collected at the TCO-coated glass substrate. The oxidized dye is regenerated by electron transfer from I^- ions, resulting in the formation of I_3^- ions. The I_3^- ions diffuse through the electrolyte and are regenerated by electron transfer from the Pt counter electrode. The overall conversion efficiency (η) of a solar cell is the product of the light harvesting efficiency (η_h), electron injection efficiency (ϕ_{inj}), and electron collection efficiency (η_c) [15]:

$$\eta = \eta_h \phi_{inj} \eta_c \quad (1)$$

The electron collection efficiency (η_c) is determined by the performance of the DSSC anode.

TiO_2 NP film is typically employed as the photoanode of DSSCs. A solar energy conversion efficiency (η) of higher than 12% has been achieved using such anodes [16]. TiO_2 NP film provides large enough surface area for dye adsorption but has a relatively slow electron transport rate. As illustrated in Figure 1b, the slow electron transport rate is mainly ascribed to the random electron transport pathways to TCO and the multiple trapping/detrapping events that occur within a huge number of grain boundaries. Moreover, electrons in the trap states suffer from significant recombination with oxidized dyes and redox species in the electrolyte if the electron detrapping rate is slow. The slow electron transport rate and significant electron recombination limit the electron diffusion coefficient and therefore the effective electron diffusion length in the photoanode [17–22].

Hierarchically nanostructured photoanodes

The electron transport/recombination properties in the photoanode determine not only the charge collection efficiency (η_c) but also the useful thickness of the DSSC photoanode. That is, the light harvesting efficiency (η_h) of the DSSC is influenced by the photoanode thickness. To further increase the optical length in the photoanode, an additional scattering layer, which comprises particles with sizes of 100–400 nm, has been introduced on top of the TiO_2 NP film [23–26]. As shown in Figure 1c, a photoanode composed of a light scattering layer constructed on top of the ordinary anode with a thickness comparable to the effective electron diffusion length has been developed to enrich the light harvesting efficiency (η_h) of the photoanode with high electron collection efficiency (η_c). Numerous hierarchically nanostructured anodes have been constructed, exhibiting a high surface area for dye adsorption and the ability to scatter light [27–31].

On the other hand, an improvement in DSSC efficiency has been expected by replacing the NP film with a vertical single-crystalline nanowire (NW; i.e., long nanorod) array, as shown in Figure 1d, for enhancing the electron transport rate. However, the performance of NW-based DSSCs is limited by an insufficient surface area for dye adsorption, even though the electron diffusion coefficient in NWs is significantly larger than that in NP films [32–36]. In order to increase the light harvesting efficiency (η_c) of NW-based