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Synthesis of TiO_2 microspheres building on the etherification and its application for high efficiency solar cells

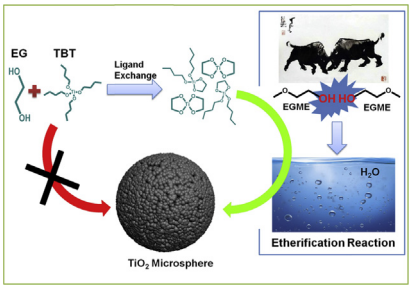
Shi-Dong Liu [a], Ying-Ke Ren [a], Zheng Zhou [a], Wang-Chao Chen [b], Zhao-Qian Li [b], Fu-Ling Guo [b], Li-E Mo [b], Ji-Huai Wu [c], Lin-Hua Hu [b, **], Song-Yuan Dai [a, b, *]

[a] Beijing Key Laboratory of Novel Thin-Film Solar Cells, North China Electric Power University, Beijing, 102206, PR China
[b] Key Laboratory of Novel Thin-Film Solar Cells, Institute of Applied Technology, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei, Anhui, 230031, PR China
[c] Institute of Materials Physical Chemistry, Huaqiao University, Quanzhou, 362021, PR China

HIGHLIGHTS

- TiO_2 microspheres were synthesized by one-pot solvothermal method.
- Etherification reaction of EGME was first demonstrated in the presence of TBT.
- Ethylene glycol was employed to control the synthesis of TiO_2 microspheres.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper describes a facile solvothermal method to synthesize TiO_2 microspheres by employing ethylene glycol monomethyl ether and ethylene glycol as solvent. By analyzing the resulted supernatant after reaction, it was proved that the etherification reaction of glycol monomethyl ether and the ligand exchange between ethylene glycol and tetra-*n*-butyl titanate played a key role in synthesis of TiO_2 microspheres. These as-obtained TiO_2 microspheres exhibited high specific surface area up to 113.24 $m^2 g^{-1}$ and have a narrow pore size distribution (6.94 nm). When applied to the photoanode, the TiO_2 microsphere-based dye-sensitized solar cells achieved a high power conversion efficiency up to 10.25%.

1. Introduction

Hierarchical TiO_2 micro-/nano-materials presented fascinating properties featuring high specific surface areas, controllable structure and variable particle sizes [1–4], which showed great potential in catalysis [5,6], lithium ion batteries [7], chemical sensors [8], water splitting [9] and especially, dye-sensitized solar cells (DSSCs) [3,10–12]. As the photoanode in DSSCs, hierarchical TiO_2

* Corresponding author. Key Laboratory of Novel Thin-Film Solar Cells, Institute of Applied Technology, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei, Anhui, 230031, PR China.
** Corresponding author.
E-mail addresses: lhhu@rntek.cas.cn (L.-H. Hu), sydai@ipp.cas.cn (S.-Y. Dai).

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materials showed better performance in specific surface area, light scattering effect and electron transport ability compared to TiO_2 nanoparticles materials [13–17]. For example, based on the aldol condensation reaction of acetone, Li et al. [14] synthesized mesoporous TiO_2 microspheres, and successfully applied it to DSSCs. The results showed that microspheres-based DSSCs exhibited outstanding characteristics including higher dye-loading capacity, stronger light scattering effect and longer electron lifetimes compared with nanoparticles paste, and the power conversion efficiencies (PCE) of cells were up to 10.32%.

Owing to the beautiful performance in materials fields, many efforts have been made to develop the synthesis methods of TiO_2 materials with hierarchical structures, including templating method [18,19], aerosol-assisted self-assembly method [20,21], hydrothermal or solvothermal method [22] and so on. For instance, by controlling the precursor hydrolysis rate and the surfactant aggregation, Sun et al. [22] synthesized hierarchical spherical dendritic TiO_2 composed of rutile nanorods, nanoribbons or nanowire subunits. Whereas, previous reported approaches often faced some challenges. For example, templating methods using either soft or hard template would inevitably produce mechanically fragile materials during template removal process [23,24]. Sol-gel process combining with a solvothermal treatment was usually considered as a complex method [1,16]. Therefore, in recent years, template-free one-pot solvothermal approaches have attracted numerous attention and been used to synthesize micro-/nano-materials, such as TiO_2 [25], ZnO [26], Fe_3O_4 [27]. For example, Jin et al. [25] prepared hierarchical nanosheet-constructed yolk–shell TiO_2 microspheres by one-pot template-free solvothermal alcoholysis process using tetraethylenepentamine as the structure directing reagent. By solvothermal treatment of $FeCl_3 \cdot 6H_2O$, urea and PEG-2000 in ethylene glycol solution at 200 °C for 48 h, Zhang et al. [27] synthesized mono-dispersed hollow Fe_3O_4/C spheres with small particles and 750 nm in diameter. These products both exhibited excellent cycling and rate performance as anode material for lithium ion batteries.

Etherification reaction of alcohols can release water in the solvothermal process, so it was widely applied to synthesizing hierarchical spherical TiO_2 [6,28,29]. For instance, Jin et al. [28] reported that the nanorods chains-constructed TiO_2 hollow microspheres were prepared based on the etherification of isopropanol. Built on etherifying reactions between alcohol and glycerol, Li et al. [6] reported the synthesis of hollow titania spheres with tunable interior structure and urchinlike morphology and demonstrated their photocatalytic activity enhanced by such unique structure. Due to the fast hydrolysis rate of Ti complexes, it was often difficult for the sol-gel methods to synthesize well-dispersed, uniform hierarchical TiO_2 materials. Therefore, spherical TiO_2 were usually synthesized in the presence of some chelating agents [30–34] (e.g., acetylacetone or ethylene glycol) to retard the hydrolysis of alkoxides and achieve control of the material properties. Ethylene glycol is a kind of useful common solvent and has been used to synthesize micro-/nano-materials, such as TiO_2 [30–32], AgCl [35], Bi_2MoO_6 [36]. At the same time, ethylene glycol can form glycolates or alkoxides/glycolate mixtures when mixed with titanium alkoxides by the ligand exchange [30–32]. Hence, the employment of ethylene glycol can control the hydrolysis rates of titanium alkoxides and generate spherical titania through a homogenous nucleation and growth process.

Inspired by above ideas, in this work, we devised a one-pot synthesis strategy to prepare TiO_2 microspheres by introducing ethylene glycol monomethyl ether and ethylene glycol as solvent. The reaction mechanism was also analyzed and confirmed by ESI-MS, FTIR and ^{1}H NMR. Finally, the TiO_2 microspheres was applied to the photoanode in DSSCs. Compared with TiO_2 nanoparticles paste (20 nm) (NP-20), the TiO_2 microspheres based DSSCs exhibited better performance, e.g., stronger light scattering and higher dye adsorption capacity, leading to a high PCE value up to 10.25%.

2. Experimental

2.1. Preparation of TiO_2 microspheres

The TiO_2 microspheres (TiO_2MS) were prepared *via* template-free one-pot solvothermal method. In a typical synthesis, 40 mL of ethylene glycol monomethyl ether (EGME) was mixed with 10 mL of ethylene glycol (EG) and this mixed solvent was stirred at ambient temperature for 15 min. As for this solution, 2 mL of tetra-*n*-butyl titanate (TBT) was rapidly added. After stirring for 5 min at ambient condition, the transparent colorless mixtures were sealed within a Teflon-lined autoclave (100 mL). After being heated at 200 °C for 12 h, the as-prepared precipitate was collected by centrifugation, washed with ethanol for several times and dried at 60 °C.

When utilized to photoanode in DSSCs, the TiO_2 materials must be annealed at high temperature to remove the organic additives used in the paste. Therefore, to characterize the properties of the microspheres after sintering, we annealed the as-obtained spheres at 500 °C for 30 min under the same condition with the treatment of photoanode.

2.2. Fabrication of DSSCs

To fabricate photoanodes of DSSCs, NP-20 and TiO_2MS pastes were prepared based on the procedures described in the previous report [10]. Then these kinds of pastes were coated on FTO substrate by screen-printing technique [10,13,14]. Afterwards, the TiO_2 films were sintered at 500 °C for 30 min. When the films cooled to 100 °C, they were soaked in 300 μM **C101** dye in a mixture of tert-butanol, acetonitrile solvent and DMSO (45:45:10 by volume) overnight. The counter electrodes were prepared on the FTO glasses by spreading out H_2PtCl_6 isopropyl alcohol solution (5 mM), followed by heating at 450 °C for 30 min in air. Finally, sandwich-type DSSCs were constructed by assembling the dye-loaded photoanodes with Pt/FTO counter electrode and the electrolyte consisting of 1 M DMII, 50 mM LiI, 30 mM I_2, 0.5 M tert-butylpyridine, and 0.1 M GuNCS in a solvent mixture of 85% acetonitrile by volume.

2.3. Characterization

The Scanning Electron Microscopy (SU8020, Hitachi, Japan) and Transmission Electron Microscopy (JEM-2100F, JEOL, Japan) were utilized to investigate morphology and size of the samples. The crystal phase and sizes of the resulting TiO_2 microspheres were characterized by the X-ray Diffraction (X′ Pert, PHILIPS, Holland) with Cu Kα radiation (λ = 1.5406 Å). The specific surface area and pore size distributions were determined by Brunauer–Emmett–Teller N_2 adsorption-desorption apparatus (BELSORP MINI II, BEL, Japan). Ultraviolet–visible (UV–Vis) spectrophotometer (U-spectrophotometer 3900H, Hitachi, Japan) was used to measure diffuse reflectance spectra and evaluate dye-loading capacity of the photoanode films. The thicknesses of TiO_2 films were examined by a profilometer (XP-2, AMBIOS Technology, USA). Resulted supernatant after reaction was filtered to remove any remaining particles and then analyzed by Electrospray Ionization Mass Spectrometry (ESI-MS) (GCT Premier, Waters, USA), Fourier Transform Infrared Spectrometer (FTIR) (IS50R, Thermo fisher, USA) and ^{1}H NMR (Advance 400 spectrometer, Bruker, USA).