Investigation of SnO2 micro/nanostructures as a photoanode material for dye-sensitized solar cell applications

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学 位 論 文 要 旨

Abstract of Doctoral Thesis

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論文題目：
色素増感太陽電池応用のための二酸化スズマイクロ・ナノ構造に関する研究

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Abstract：

With depletion of nonrenewable sources, the need for renewable energy is in demand. Sun's energy is abundant in nature. Recent advances in developing solar cells aim for a long, stable and low cost device. Third generation photovoltaics consisted of dye sensitized solar cell (DSSC) which is an alternate for the Si based cells. Although the efficiency is less compared to Si based cells, DSSC is attractive due to cost effective and easy fabrication. DSSC is consisted of FTO (Fluorine doped tin oxide) as working electrode, dye sensitized oxide film coated on FTO, a Pt: FTO as counter electrode, and an electrolyte based on iodide/tri-iodide between electrodes. Most of the materials in DSSC are wide band gap metal oxides such as TiO_2, ZnO and SnO_2. Widely used materials are based on TiO_2 or ZnO which produced higher efficiency compared to other oxides. Although TiO_2 based cells showed the highest efficiency of 15 %, the drawbacks like lower electron mobility and poor stability have directed research towards SnO_2 based DSSC. Various factors affecting the performance of SnO_2 include faster recombination between dye molecules and iodide/tri-iodide which limits the fill factor (FF) and open circuit voltage (V_{oc}). An another factor is high overpotential at dye/oxide interface. SnO_2 has larger band gap of 3.6 eV than TiO_2 (3.2 eV) and ZnO (3.35 eV). SnO_2 has good photo stability under UV, optical transparent in visible region, higher electron mobility and lesser degradation of dye which make it an alternate material for photoanode but still the performance is lower than TiO_2. Thus, further improvement of SnO_2 based materials is required for better performance in DSSC. The objective of this research is (1) to synthesize various SnO_2 structures (microspheres, nanoparticles), and composites (Zinc tin oxide nanocubes) by the

hydrothermal method. (2) To fabricate DSSC using synthesized SnO_2 materials by doctor blade method. SnO_2 mesoporous microspheres were synthesized by hydrothermal method. Triethylamine (TEA) acted as a capping ligand. Structural characterizations like X-ray diffraction (XRD) and Raman spectra confirmed that both uncapped and capped SnO_2 had rutile phase. Presence of TEA was confirmed by Fourier transform infrared (FTIR) spectroscopy. Field emission scanning electron microscope (FESEM) showed that, with an addition of TEA, number of nanoparticles on surface of microspheres were increased. Microspheres of average diameter of 2-2.5 μm and nanoparticle of 20 nm size were formed. Brunauer-Emmett-Teller (BET) showed that the SnO_2 had mesopores. The surface area was increased for TEA-capped SnO_2. Uncapped and capped SnO_2 were coated on FTO by doctor blade method and immersed in N719 dye. 50 mM redox electrolyte solution was used. I-V analysis were performed for both cells. TEA capped SnO_2 showed higher efficiency of 1.67 % than uncapped SnO_2 (efficiency of 0.97%) because of higher surface area, dye absorption and incident photon to current conversion efficiency (IPCE).

Novel morphology of SnO_2 similar to sugar-apple shape was obtained without urea by the hydrothermal method. Morphological changes were seen with the addition of urea. Novel structure and urea assisted SnO_2 showed rutile phase from XRD and Raman spectra. FTIR confirmed the presence of urea. FESEM showed that the microspheres were 2-3 μm with light scattering ability at 400 to 800 nm. The addition of urea changed pyramid facets (210 nm) to nanoparticles (22 nm) as confirmed by transmission electron microscopy. DSSC photoanode was coated using doctor blade method and dipped in N719 dye, with 50 mM redox electrolyte and 60 μm spacer. The photoanode materials were coated as scattering layer on P25 layer of 4 μm. The higher efficiency of 2.76 % was obtained for P25/sugar apple SnO_2 composite with 22.81 ms recombination rate compared with SnO_2 microspheres. Thus, this novel shape acted as a scattering structure which enhanced the performance of cell.

Ternary oxides like Zinc tin oxide (ZTO) was synthesized using the hydrothermal method and different annealing temperature helped to analyze the phase involved in formation of nanocubes. Average size of ZTO nanocubes was 80-100 nm. XRD showed different phases of ZTO for each annealing temperature. From thermogravimetric-differential thermal analysis (TG-DTA), ~ 18 % weight loss occurred between 200-280 °C. The phase transformation was studied by annealing ZTO of 100 – 750 °C. $ZnSn(OH)_6$ (ZHS) was formed at 250-550 °C. It showed metastable $ZnSnO_3$ and recrystallized to Zn_2SnO_4 phase above 650 °C. TEM and EDS mapping for all the phases were studied. ZHS and P25 composites were coated on FTO. The highest efficiency of 3.56 % was obtained for P25/ZHS nanocubes with N719 dye, 50 mM iodide electrolyte and 60 μm spacer.

The above results show that SnO_2 can be used as an alternate for photoanode materials.