Lanthanum doped TiO_2 mesoporous spheres as photoanode for DSSC applications

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1. Introduction

Since first proposed by O'Regan and Gratzel, Dye-Sensitized Solar Cells (DSSCs) has gained a lot of attention due to its simplicity and low-cost fabrication technique. It is typically made up of fluorine-doped tin oxide (FTO) layer, photoanode, dye, hole transporting material (HTM) and counter electrode. The photoanodes are typically made up of wide band gap semiconductors like TiO_2 and ZnO. The TiO_2 is most commonly used photoanode for DSSCs application due to its strong affinity for organic molecules, similar band alignment with commonly used dyes, non-toxicity, low-cost and photostable. One method of increasing efficiency of DSSC is by increasing dye concentration on TiO_2 photoanode. Generally, a dye molecule attaches to surface Ti atoms, hence, dye loading can be increased by increasing oxygen vacancies on TiO_2 surface. In order to create more oxygen vacancies on surface of TiO_2, Lanthanum-doping into the TiO_2 crystal structure was performed. Typically, the La-O bond is stronger than the Ti-O bond. Thus, it can extract oxygen atoms from TiO_2 and create oxygen vacancies in the process.

2. Experimental method

3 mL of titanium tetraisopropoxide was dissolved in 150 mL of ethylene glycol and kept overnight stirring. To the above solution, 300 mL of acetone and 3 mL of deionized water were added. After additional stirring for 2 h, white suspension was formed. The suspension was centrifuge and collected precipitates were washed with water and ethanol, followed by drying the sample at 100 °C for 10 h. 1g of prepared mesoporous TiO_2 powder was dispersed in 100 ml of deionized water and $La(NO_3)_3.7H_2O$ (1 mM, 2 mM, 3 mM, 4 mM and 5 mM) was added and kept for overnight stirring. The solution was transferred to a 100ml Teflon lined stainless steel autoclave and kept in a furnace at 160 °C for 12 h. The resulting product was centrifuged, washed, with water and ethanol, and dried at 100 °C for 10 h. After drying, samples were annealed at 350 °C for 2 h. The samples were dissolved in ethanol and was grounded by ultrasonicated for 30 min. A few drops of Triton-X was added as binding agent. The solutions were then sprayed on FTO glass substrate at 150 °C by spray pyrolysis. These sample-coated FTO glass were then annealed at 450 °C for 2 h. The resulting photoanode was the submerge in ethanol solution containing 0.03M of N719 or D205 dye for 15 h. The photoanode was clamped with Pt coated glass and electrolyte was filled between to form sandwich type cell. Similar steps were taken to fabricate P25 Titania powder coated DSSC.

3. Results and discussion

The XRD spectra (Fig 1) shows that anatase phase of TiO_2 and rhombohedral phase of $LaTi_{21}O_{38}$ are present in all samples with different concentration of Lanthanum. The presence of Lanthanum was confirmed using XPS analysis. The XPS analysis also shows that Ti^{3+} and adsorbed oxygen is present in all the samples which suggests the presence of oxygen vacancies in the samples. The FESEM, EDAX and HRTEM analysis shows that Lanthanum is incorporated on the surface of mesoporous TiO_2. The elemental mapping shows that Lanthanum is uniformly distributed over the surface of TiO_2. The I-V characteristics shows that samples with 3 mM of Lanthanum showed best efficiency of 4.45% (D205 dye) and 4.26% (N719 dye) over the pure TiO_2.

4. Summary

La-doped mesoporous TiO_2 with varying concentrations were successfully synthesized by solvothermal method. The XPS analysis confirmed the presence of lanthanum in all the samples. The XRD shows presences of pure anatase phase of the TiO_2 and rhombohedral phase of $LaTi_{21}O_{38}$. The FESEM images of the samples confirms the mesoporous morphology of TiO_2. The FESEM and EDAX also shows that Lanthanum is covering around mesospheres and is distributed uniformly. The La-doped TiO_2 was used to successfully fabricated DSSC using two different dyes - N719 and D205. The highest efficiency of 4.45 % and 4.26% was obtained for sample with 3 mM Lanthanum with D205 dye and N719 dye respectively.

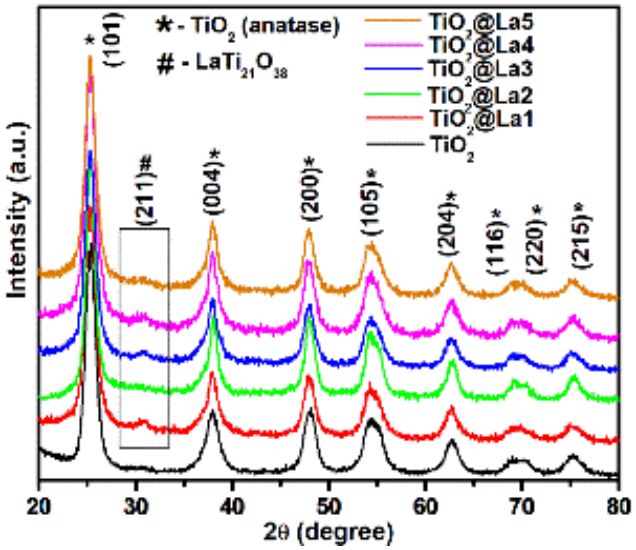

Figure 1. XRD spectra of sample with different concentration of Lanthanum