



Photoexcitation of neodymium doped TiO₂ for improved performance in dye-sensitized solar cells



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ABSTRACT

A series of Nd-doped TiO₂ with Nd content ranging from 1 to 5 at.% were synthesized by solid state technique and explored as a photoanode material in dye-sensitized solar cells (DSSCs). Incorporation of Nd³⁺ into TiO₂ lattice resulted in more negative flat band potential for Nd-doped TiO₂ than pure TiO₂, as determined by impedance spectroscopy (Mott–Schottky plots), which is highly desirable to achieve higher V_{oc} in DSSCs. In addition, Nd doping in TiO₂ provided the opportunities to engender higher density of oxygen vacancies and band gap narrowing in Nd-TiO₂ photoanode, which collectively enhanced the optical properties of photoanode DSSC in terms of higher dye loading and light absorption respectively. A best efficiency of 6.17% was achieved with 4% Nd-doped titania, resulting in a remarkable increase in efficiency (102.3%) of the device over the undoped titania cells. Induction of intermediate bands, realignment of energy levels leading to a better electron injection, high sensitizer loading, efficient charge separation due to dopant and its impurity levels contribute favorably towards the superior performance of Nd doped TiO₂ DSSC. Spectroscopy (EIS) measurements showed Nd doped TiO₂ photoanode possessed higher charge recombination resistance and longer electron lifetime compared to DSSCs with undoped TiO₂.

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1. Introduction

Dye sensitized solar cells (DSSCs) that use dye molecules to absorb photons and convert them to electric charges, have drawn extensive attention due to their ease of device making, low cost and their comparatively better energy-conversion efficiency [1–3]. A conventional DSSC made of a dye-activated mesoporous semiconductor oxide film on conducting glass, an iodine electrolyte solution, and a platinised counter electrode [4]. Contradictory to typical silicon solar cells, wherein the semiconductor takes charge of both the photon absorption and charge transport, in DSSCs, light is absorbed by the sensitizer (dye) and allows electron injection from the sensitizer to the conduction band of the semiconductor. There are several ways to enhance the performance of DSSCs namely by (a) increase of light harvesting, which could be achieved by good surface area, and absorption of broader range of solar light [5]; (b) increase of the electron injection speed by improving the electron injection over potential [6,7]; (c) moving the redox couple Fermi level to enhance the dye regeneration rate [8,9]; (d) enhancing the lifetime of electrons by retarding the probability of charge recombination [10]; and (e) improving the charge transfer rate in TiO₂ [11,12].

Appropriate improvement of the photoanode, more so the modification of the nanoparticles (NPs) used in working electrode can exhibit a relatively strong capability to meet all the above criteria via a tailored microstructure of semiconductor NPs which excels in light harvesting, electron injection, electron transport and charge separation [13]. TiO₂, in special, is a broadly accepted material as a good electron transport and separation medium for DSSCs in which the voltage occurs at the interface between the dye-sensitized metal oxide semiconductor and an electrolyte [14]. TiO₂ has also been the most promising material among the other semiconductors used in DSSCs due to its exceptional properties such as good oxidative ability, strong chemical stability, being economical and possessing environment friendly features [15]. The mesoporous TiO₂ working electrodes that have percolated links of the NPs yield very high photocurrent due to their enhanced surface area apt for dye adsorption and favorable energy level alignment to allow electrons from the dye molecules to nanostructured films [16]. Doping of TiO₂ with transition metal ions can further enhance optical absorption, extend band edge energies, and increase electron density of states and favorably align Fermi levels [17–20].

Recently reports indicate that lanthanides are effective dopants for altering the crystal structure of TiO₂ due to their unique electronic configuration and spectral characteristics to achieve the above desired properties of DSSCs [21,22]. Zhang et al. [21] described that doping of

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lanthanides can cause prominent improvement in the photoresponse of TiO_2 , and this improvement was susceptible to the ionic, electronic configuration and atomic radius. Lanthanide dopants can reduce the band gap of TiO_2 and the fundamental absorption edge red-shifts to visible region, still keeping its strong redox potentials. The Ti 3d states of conduction band (CB) are split into e_g and t_{2g} states in a ligand field with O_h symmetry, and hence the CB is separated into upper and lower parts [23]. On doping of lanthanide into TiO_2 (although a nanoparticle), their 4f/5d states are more or less delocalized, thus adding significantly to form impurity energy levels (IELs), thus broadening the CB or VB [24]. This results in band gap narrowing. An enhanced utilization of the broader range of solar spectrum could be achieved with intermediate bands (IBs) formed by IELs [25]. Properly located IBs behave as stepping stones to allow low-energy photons to excite electrons from VB to CB. IBs also serve to trap and detrapp electrons thus prolonging the lifetime of charge carriers. In addition lanthanides proportionately plunder oxygen into TiO_2 lattice to cause surface oxygen vacancies for dye absorption and thus electron harvesting [26].

Doping of Sm^{3+} , Nd^{3+} , Pr^{3+} , Eu^{3+} and La^{3+} in particular could enhance the photo electrochemical properties, improve the photoresponse and the photocurrent conversion efficiency for the range 350–400 nm [27,28]. In a DSSC the power conversion efficiency (PCE) of the device is determined by the open-circuit photovoltage (V_{oc}), short-circuit photocurrent (J_{sc}), and the fill factor (FF). Nd^{3+} being a dopant induces IBs which could steeply reduce the band gap to the visible range [29–31] and allow the semiconductor to photoexcite electrons for electron transport, thus favorably influencing the density of electrons and hence J_{sc} . The mismatch of ionic radius of Nd^{3+} (0.983 Å) and Ti^{4+} (0.605 Å) tends to induce lattice distortion/defects [13]. The obtained larger diameters of doped particles can contribute to scattering of incident light [1] which can confine the incident light better and reduce the loss of photon energy [32,33] and hence enhance J_{sc} . The open circuit potential (V_{oc}) is given by the potential difference between the quasi-Fermi level of oxides and Nernstian potential of the electrolyte [34]. So, if the number of the electrons being injected is enhanced and/or loss of the injected electrons by recombination is less, V_{oc} would improve, increasing the oxide's quasi-Fermi level. Nd^{3+} doping allows feasible CB shift and engineers a more favorable equilibrium Fermi level position for an enhanced V_{oc} . The substitutional Nd^{3+} dopant thus was aimed to contribute to both an enhanced J_{sc} and V_{oc} and hence an overall efficiency of the solar cell.

The above findings inspired us to synthesize Nd doped TiO_2 NPs for application of these NPs as photoanode material for DSSCs. There have been reports on the preparation of Nd- TiO_2 by hydrothermal and solvothermal method and being utilized as the photoanode of nanostructured solar cells [35,36]. Use of chemical methods for dopants tend to cause deep dopant energy levels which may not be available for charge transfer and may also end in recombination adversely affecting the efficiency. Hence physical process of pulverization has been attempted to cause surface level doping. Significant changes in the conversion efficiency of DSSCs using different and nominal trace concentrations of Nd dopant (in TiO_2) were observed, analyzed and related to morphological, electronic and optical changes that were studied by spectroscopy and microscopy. The kinetics of charge transport and recombination rate was studied by Electron Impedance Spectroscopy.

2. Experimental

2.1. Materials and methods

All the chemical reagents were used without any further purification. $\text{Nd}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (99.9%, Loba chemicals) was used as precursor for the neodymium doping, TiCl_4 (99.5% loba Chemie) was used as a titanium source for the preparation of TiO_2 . Fluorine doped tin oxide (FTO) glass (Sigma Aldrich). The others include sulphuric acid, sodium hydroxide, ammonium hydroxide, acetic acid, ethanol were from

Merck and Triton X-100, Ruthenium 535 dye ($\text{Ru}(\text{bpy})_2(\text{NCS})_2\text{H}_4$), Iodolyte TG-50, Platisol were from Solaronix.

2.2. Preparation of TiO_2

The preparation of TiO_2 NPs is as per our earlier protocol [37]. To brief the preparation, 100 mL aliquot of TiCl_4 was added drop wise to 1 L of double distilled water with vigorous stirring and a temperature of $< 10^\circ\text{C}$, to avoid the agglomeration of NPs during hydrolysis. To complete the hydrolysis 1 mL H_2SO_4 is added followed by the addition of ammonia for precipitation till the pH reaches 7–8. The obtained precipitate was allowed to settle, washed with distilled water, filtered using Whatman 41 filter paper, dried and ground. The TiO_2 powder was annealed at 600°C for 6 h to obtain an anatase phase of TiO_2 .

2.3. Preparation of Nd doped TiO_2

Neodymium (Nd) substituted TiO_2 was synthesized by solid state technique using $\text{Nd}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ as precursor. 0.98:0.02 weight ratio of TiO_2 and neodymium oxide was used to obtain 1% Nd-doped TiO_2 . The mixture were pulverized in an agate vial using a ball mill (SPEX 8000M) for a time period of 90 min and annealed at 600°C for 6 h. Similar procedure was adopted by varying the weight ratio of the precursor and TiO_2 to obtain 2%, 3%, 4% and 5% Nd doped TiO_2 . To cause an effective doping, pulverization and annealing was repeated. Plastic deformation of TiO_2 crystal lattice takes place when it undergoes the process of milling, causing stresses and strains in the lattice. This produces lattice distortion and forms many defects inside TiO_2 particles. The high surface energy and lattice distortion energy creates activation energy for atomic and ionic diffusion at room temperature. During the process of pulverization the collision that occurs between the grains of powder and the balls of the mixer mill causes a rise in interface temperature to induce incorporation of dopants [30].

2.4. Preparation of paste and fabrication of DSSC

FTO substrate was cleaned in surfactant, deionized water, acetone and ethanol. Paste of TiO_2 was prepared with 0.25 g of TiO_2 , 0.5 mL of acetic acid and 1:1 (10 mL) mixture of deionized water and ethanol ground for 20 min. Triton-X (0.5 mL) was added, the resultant mixture was ground to get homogenous paste. Doctor blade technique was adapted to cast the TiO_2 paste on FTO glass substrate [4]. TiO_2 coated

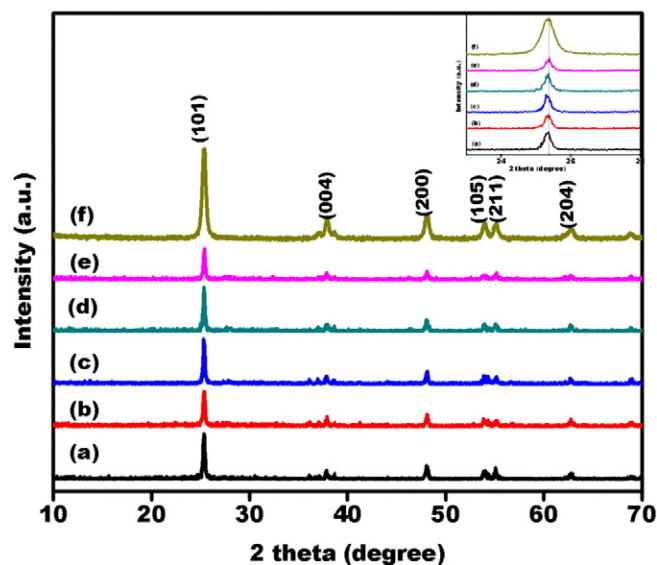


Fig. 1. X-ray diffraction pattern of (a) 1% Nd- TiO_2 , (b) 2% Nd- TiO_2 , (c) 3% Nd- TiO_2 , (d) 4% Nd- TiO_2 , (e) 5% Nd- TiO_2 and (f) TiO_2 .

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