Doped Titania Nanocrystalline Photoanodes for Efficiency Improvement of DSSCs

Di Gu[*1], Yanji Zhu[1], Qingwei Zang[2], Zhigang Xu[3], Nan Wang[3]

[1]College of Chemistry and Chemical Engineering, Northeast Petroleum University, China

[2]The Fourth Oil Extraction Plant, Daqing Oilfield Company Limited, Qaqing, China

[3]Daqing Oilfield Engineering Co. Ltd., Qaqing, China

[*1]48184820@qq.com

***Abstract*-Dye-sensitized solar cells(DSSCs) is thought to be a candidate to realize the large-scale use of solar energy for it has many advantages such as non-toxic, high efficiency of conversion, low cost, etc. The photoanode as a media of dye adsorption, electron transport, and electrolyte diffusion is the most important part of DSSCs. The composition of the photoanode of DSSCs directly influences the conversion efficiency and long-term stability. This paper studies the doped titania nanocrystalline photoanodes for efficiency improvement of DSSCs. Through the photoelectric property test of DSSCs, it is learned that Zn^{2+} doped TiO_2 photoanode with mole fraction of 0.05% has the best performance. Lastly, an outlook on the future challenge and prospects of doped nanocrystalline TiO_2 photoanode materials are also briefly brought up.**

Keywords- DSSCs; Photoanode; Doping; Concentration of Ion Doping; Photoelectric Property

I. INTRODUCTION

Dye-sensitized solar cells(DSSCs) is thought to be a candidate to realize the large-scale use of solar energy for it has many advantages such as non-toxic, high efficiency of conversion, low cost, etc. Since the DSSCs in 1991 [1] has made breakthrough progress, it has aroused widespread concern in the academic circle and the business community [2-3]. As a media of dye adsorption, electron transport, and electrolyte diffusion, photoanode is the most important part of DSSCs. The composition of the photoanode of DSSCs directly influences the conversion efficiency and long-term stability. In recent years, doping TiO_2 with metal and nonmetal elements has been considered as a promising way to tailor the electronic properties of TiO_2 photoanode in DSSCs and has succeeded in improving photovoltaic performance of DSSCs [4-5]. Performed on some of monocrystalline or polycrystalline TiO_2 doped metal ions present in the crystal lattice of the metal ion has become good electron trap can reduce electron-hole pair recombination, extend the life of charge, thereby improving the efficiency of DSSCs [6]. This paper studied the influence of different ion doping and different concentration of ion doping on the electrical and optical properties of DSSCs, and confirmed the best concentration and the best types of ion doping through optical performance testing.

II. EXPERIMENTAL

A. The Preparation of Doped Titania Nanocrystalline Photoanodes

Sol-gel method is a common method for preparing wet chemical materials. Sol-gel derived samples with high uniformity, high purity of products, easy control of the reaction process, has great advantages in the application of the film, becoming one of the most commonly used method for preparing thin films [7]. TiO_2 film composition prepared using different process methods or parameters, structure, orientation and thickness are the differences.

In this experiment, chemically pure tetrabutyl titanate as raw material, using ethanol as solvent, diethanolamine as complexing agent, nitric acid as catalyst. Experiment steps are as follows:

(1) Prepare a mixture A with tetrabutyl titanate, ethanol and diethanolamine, fully stirred to give a homogeneous mixture.

(2) Prepare a uniformly mixed mixture A with ethanol, deionized water and nitric acid.

(3) Under magnetic stirring, the above mixture B was added into the mixture A dropwise to obtain a uniform, light yellow transparent sol, and the hydrolysis polycondensation reaction at room temperature to obtain sol C.

Containing the desired ionic salts were put into B solution, under magnetic stirring, the mixture B containing the desired ions in the mixture A was added dropwise to give a homogeneous, light yellow transparent sol, and it a hydrolysis polycondensation reaction to obtain a sol C at room temperature.

B. The Preparation of DSSCs

The TiO_2 film was prepared by sol-gel method, annealing in a muffle furnace. After hydrolysis of the intermediate product suitable high-temperature annealing was completely decomposed, residual organic matter can be completely removed, and finally completely dehydrated, only closely integrated with the substrate of titanium dioxide films.

The counter electrode was prepared by electroplating method on FTO conductive glass with pt. Eosin Y as sensitizer.

III. RESULTS AND DISCUSSION

C. Effect of Different Ion-doped Optical Performance of DSSCs

Testing the DSSCs with Beijing Changtuo Company CHF-XM-500W xenon lamp as the light source, the incident light intensity was 73.1mW/cm^2. The open circuit voltage can be seen from Table 1, Nd^{3+} doped TiO_2 thin films was lower, Zn^{2+} doped TiO_2 thin film photovoltaic best performance, cell power was the highest, indicating that the effect of doping of Zn^{2+} was the best.

TABLE 1 DSSCS PHOTOVOLTAIC PERFORMANCE TEST RESULTS OF DIFFERENT DOPED

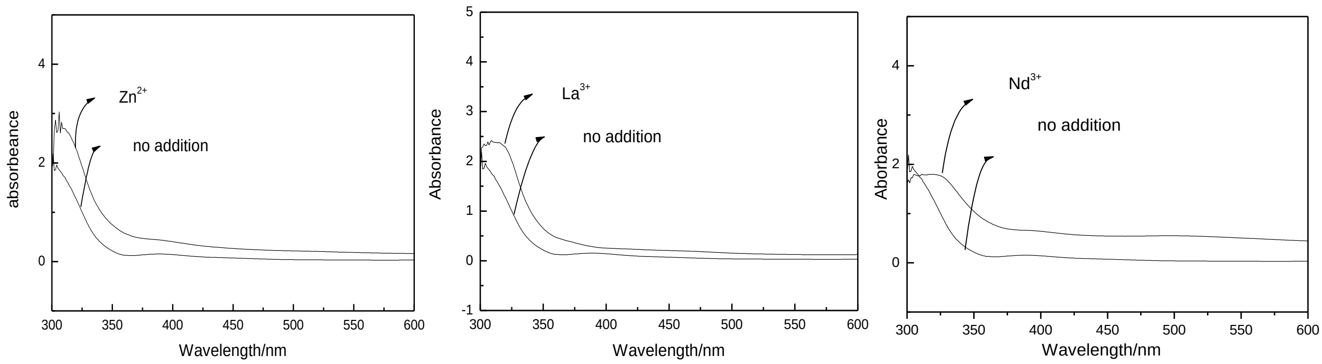
concentration of the doping	concentration of the doping	concentration of the doping	concentration of the doping
Zn^{2+}	0.632	0.605	0.163
La^{3+}	0.624	0.459	0.116
Nd^{3+}	0.533	0.601	0.122
No doping	0.565	0.250	0.066

As can be seen from the Table 1, not only the curve hardness of ion-doped TiO_2 film was significantly better than undoped TiO_2 film, but also the current and voltage was higher than the undoped film when you connect the load. Confirm the truth of certain concentration of doping ions can improve the photocatalytic activity of TiO_2 thin films. This was because the oxide melting point has a certain influence on the phase transformation of TiO_2, it can inhibit the transformation of anatase to rutile when the oxide melting point was higher than TiO_2 and can promote the transformation when the oxide melting point lower than TiO_2, and the lower melting point effect more obvious. In addition, doping ions proned to redox reaction in the titania lattice surface, then produced oxygen vacancy or interstitial titanium by diffusion, thereby inhibiting the interaction between different titanium atoms, transition hinder anatase to rutile phase, to improve the light absorption ability of TiO_2 thin films.

D. UV-Vis Characterization of Different Ion Doped TiO2 Thin Film

The characteristics of samples were examined through a uv-vis spectrophotometer type UV-2550 produced by Japanese Shimadzu Company, the scan speed was medium, the slit width was 2nm, and the wavelength range was 300nm to 800nm.

Fig. 1 was the UV-Vis spectra of TiO_2 films doped with ions in the 300-600nm. It can be seen from that the spectra in the wavelength range of 500nm or more, whether the TiO_2 film was doped with ions or not, light absorption was relatively small. The maximum absorption peak at 300-400nm, and the wavelength was shifted to shorter wavelength direction as the absorption peak was more obvious. While in the UV range, TiO_2 films have a strong absorption of light.



(a) (b) (c)

(a) UV-Vis spectra curve of Zn^{2+} doped TiO_2 thin film
(b) UV-Vis spectra curve of La^{3+} doped TiO_2 thin film
(c) UV-Vis spectra curve of Nd^{3+} doped TiO_2 thin film

Fig. 1 UV-Vis spectra curve of ions doped TiO_2 thin films

The spectral curve changed on the form compared with the non-doped TiO_2 films. The absorption peak shifted to longer wavelengths, spectral red shift. Expand the scope of TiO_2 nanoparticles in response to visible light direction, improved the absorption properties in a certain extent. The band gap of TiO_2 film doped with Zn^{2+} is 2.77eV, doped with La^{3+} is 2.51eV, doped with Nd^{3+} is 2.71eV, all of those is smaller than the band gap of undoped TiO_2 films(3.0eV), demonstrating that the doping ion can improve the photocatalytic activity of TiO_2 thin films.

E. Effects of Doping Concentration on the Photoelectric Properties of DSSCs

Many studies have shown that ion doping with an optimal concentration. With increasing the concentration of the doping, the surface space charge layer is narrowed, electrons and holes are generated by light excitation TiO_2 and can be effectively separated, the lifetime of photo-induced carriers prolonged, but when the doping concentration is lower than the optimal concentration, there is not enough traps in the semiconductor to capture the photo-induced carriers, electrons and holes cannot reach the most effective separation. When the optimum doping concentration, the space charge layer thickness is exactly equal to the incident light penetration depth, the photo-generated electrons and holes have the optimal separation, the most favorable to the photocatalytic reaction; It would cause an increase of photo-induced carriers recombination in the surface when excess dopant to reduce the photocatalytic efficiency.

The doping of Zn^{2+} as an example, illustrates the effects of different doping concentration on the properties of DSSCs. The doping concentration in solution was 0.001%, 0.03%, 0.05%, 0.1%, 0.2% (mole fraction), respectively. As can be seen from Table 2, the open circuit voltage and short circuit current increased with the ions concentration increased. However, when reached a certain value, the open circuit voltage and short circuit current decreased, which also proved the existence of an optimum value of ions concentration, and the optimum value was 0.05%.

TABLE 2 PHOTOVOLTAIC PERFORMANCE OF DIFFERENT CONCENTRATIONS IONS DOPED DSSCS

Mole Fraction/%	**V_{oc}(mV)**	**I_{sc}(mA/cm^2)**	**P_{max}(mW/cm^2)**
0.001	540	0.444	0.086
0.03	580	0.524	0.109
0.05	632	0.605	0.180
0.1	580	0.564	0.122
0.2	560	0.403	0.097

F. UV-Vis Spectra of Different Concentration Ion Doped TiO2 Thin Film

Fig. 2 was the UV-Vis spectra of TiO_2 films doped with Zn^{2+} between 300nm and 600nm, including1,2,3,4,5 respectively represent the doping concentrations were 0.001%, 0.03%, 0.05%, 0.1%, 0.2%(mole fraction). Asit can be seen from the spectra, the shape of the curve changed with increasing the concentration, the absorption peak shifted to longer wavelengths. However, the concentration continues to increase, the absorption peak moves to shorter wavelength. It also showed the presence of an optimum doping concentration, and the most preferably concentration of 0.05% (mole fraction). This was consistent with previous analyses. It presented the first band gap decreased after the increase. It also showed that there was an optimal doping concentration. The band gap of the mixture narrowed compared with pure TiO_2, the right concentration of Zn^{2+} doped TiO_2 improved ability to absorb long-wave photons.

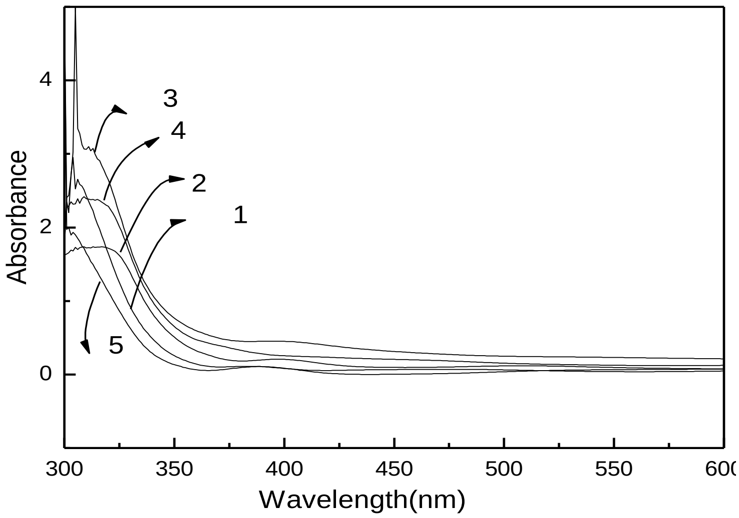


Fig. 2 UV-Vis spectra of different concentrations of ions doped TiO_2 thin films

IV. CONCLUSIONS

This paper studied the doped titania nanocrystalline photoanodes for efficiency improvement of DSSCs, through the photoelectric property test of DSSCs.

(1) Experimented study of Zn^{2+}, La^{3+}, Nd^{3+} three kinds of ion doping on photoelectric properties of TiO_2 films, and the

results showed that Zn^{2+} doped TiO_2 photoanode with mole fraction of 0.05% has the best performance. The UV-Vis spectra of doped TiO_2 also confirmed this conclusion.

(2) Based on the test results, main reasons of the doped TiO_2 improving optical properties of DSSCs were: doping changes the conduction band of TiO_2 position; doping improves the transmission rate of TiO_2 electronic; doping reduces the complex reaction of TiO_2/electrolyte interface and TiO_2/dye; doping increases the dye adsorption capacity; doping enhanced the absorption of visible light of TiO_2.

(3)Future research should focus on the doping mechanism, through in-depth study of the mechanism, to avoid adverse effects on the DSC doping elements brought to more effectively improve the photoelectric conversion efficiency of DSSCs.

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