In this survey, N, La co-doped TiO2 nanocrystals are synthesized through simple sol–gel method. Results reveal that both elements of N and La are introduced successfully into the structure of TiO2 and exist as the form of La2O3 and TiO2–La2O3. The efficiency was found to be 4.81%, which was affected by both optoelectronic and microstructural properties. The maximum value of Jsc reached 5.18%. Qin et al.19 prepared N-doped TiO2 samples by wet method with urea as nitrogen source and applied them to low-temperature DSSCs, and the maximum value of Jsc reached 5.18%. The efficiency was found to be 0.104%. An’amt et al.20 synthesized Bismuth–TiO2 nanocubes via a facile sol–gel hydrothermal method at low temperature, the n was found to be 2.11%. Salavati-Niasari et al.21 deposited CdS on TiO2 using successive ion layer adsorption and reaction, the n was 4.50%.

Herein, in our survey, we aim at enhancing the Jsc values significantly by combining rare-earth metal elements of La and N doped in TiO2 materials to improve the efficiency of the low temperature-based DSSCs. Recently, Wang et al.22 studied the optical properties of N, La co-doped anatase TiO2 via calculation, which is based on the density functional theory. They reported that after N and La atoms are codoped into anatase TiO2, there are some significant changes in the electronic density. When an O atom is replaced by an N or La atom, the charge distribution of the system is correspondingly changed. Thus, the electrons of higher electronic density can easily obtain smaller energy and enter into a lower energy region when the holes are left in their original positions, which are beneficial for the separation of photogenenerated electrons and holes and useful for enhancing photo activity.23 Simultaneously, the dipole moment of a distorted octahedron can induce the local internal fields after doping N,La. Dye-sensitized solar cells (DSSCs) have attracted a lot of research interest due to the low-cost, easy fabrication, good stability, and high photoelectric conversion efficiency.1 However, the traditional fabrication procedure of DSSCs requires not only the heavy FTO substrate, but also a high temperature calcination process at about 500°C. These will limit the large area production and commercial application of DSSCs. In order to overcome these problems, flexible DSSCs with their incomparable advantages have attracted more interest of scientists,2 compared with the traditional high temperature-based DSSCs. By using the flexible substrate, the high temperature calcination process is not needed, which can save energy and reduce the production cost. More importantly, a wide range of flexible substrates can be applied in the fabrication of flexible DSSCs. Generally, the transparency of the solar cell substrate need to be more than 80%, and thus only FTO can be employed in the high temperature-based DSSCs. For the low temperature-based DSSCs, the substrate can involve FTO, ITO-PET (ITO-coated pol(ethylene terephthalate), ITO-PEN (ITO-coated polyethylene naphthalate), Ti foil and Ti meshes,3,4 ZnO/Al thin film with high transmittance,5 etc. It is believed that the cell based on the flexible substrate should possess the merits of being light weight, foldable and easy to carry, and thus can be used in portable electronic products. Furthermore, the cell preparation process is simple and suitable for industrial roll-to-roll mass production. It is known that the fabrication of photoanode at low temperature is essential for these flexible DSSCs. The paste employed for the generation of photoanode does not have to undergo a high temperature (about 500°C) annealing process, since no organic materials are introduced. After a slight agitation, the paste could be dried at low temperature(<150°C). Unfortunately, it is reported that the short-circuit current (Jsc) is low without the high temperature calcination process, which is the main reason for the poorer efficiency realized by this method.4 However, the efficiency of the cell prepared by this method is still far from the practical application. Meanwhile, it is a pity that the most efforts of scientists are only devoted to the strategies of fabricating the photoanode of DSSCs, few is attempted to improve the Jsc values by employing other strategies in the field of low temperature-based DSSCs. It is well known that doping TiO2 with nonmetal elements (such as nitrogen, carbon, sulfur, boron and phosphorus) could improve the light absorption in the visible region and greatly enhance the short circuit current of DSSCs.10 Among those doping nonmetal elements, N is found to be more promising.13 It was reported that TiO2 nano-material doped with rare-earth metal element could also improve the short circuit current of DSSCs by reducing the recombination rate of photogeneneration-electron-hole pairs and enhancing separation efficiency of charge carriers.14 As a rare-earth metal element investigated widely, lanthanum is effective to improve the photoelectric activity of TiO2.16 Actually, there are few reports about doped TiO2 for use in low temperature-based DSSCs. Ting et al.17 synthesized TiO2 mesoporous beads doped with N by using a microwave-assisted method and fabricated low temperature-based DSSCs, the n was found to be 4.81%, which was affected by Jsc. Chen et al.18 synthesized N-doped TiO2 samples by wet method with urea as nitrogen source and applied them to low-temperature DSSCs, and the maximum value of n reached 5.18%. Qin et al.19 prepared N-doped TiO2 photoelectrodes on titanium sheet at low temperature by micro-plasma oxidation method in electrolyte with (NH4)2SO4 and NH3·H2O as nitrogen sources, respectively. However, the efficiency was found to be only 0.104%. An’amt et al.20 synthesized Bismuth–TiO2 nanocubes via a facile sol–gel hydrothermal method at low temperature, the n was found to be 2.11%. Salavati-Niasari et al.21 deposited CdS on TiO2 using successive ion layer adsorption and reaction, the n was 4.50%.

© The Author(s) 2016. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0141610jes] All rights reserved.
element and a larger dipole moment of TiO₂ octahedron causes higher absorption coefficient in the visible-light region. All of these could be helpful for the optical properties of N, La-codoped TiO₂. Therefore, we synthesize N, La co-doped TiO₂ powder using urea and lanthanum nitrate as the dopants. The resulting doped samples are applied in the fabrication of the photoanodes of low temperature-based DSSCs. The highest temperature of the whole process was only 120°C. To the best of our knowledge, this is also the first report for the fabrication of low temperature-based DSSCs employing N, La co-doped TiO₂ nanocrystals as photoanodes, whose performance was compared with DSSCs fabricated with pure TiO₂, La-doped TiO₂ and N-doped TiO₂ samples. As expected, N, La co-doped TiO₂-based solar cell exhibited higher J_sc than pure and single element-doped TiO₂-based DSSCs.

**Experimental**

**Main materials.**—Urea (CO(NH₂)₂) and lanthanum nitrate (La(HNO₃)₃·6H₂O) are purchased from Tianjin Kemioiu Chemical Reagent Co., China. Tetrabutyltitanate, absolute ethanol, isopropanol and ammonia (NH₄OH) are from Guangfu Chemical Reagent Co., China. Titanium tetraisopropoxide (TTIP) is purchased from Liyuan Chemical Reagent Co., China. 1,2-dimethyl-3-propylimidazolium-iodide (DMPII), LiI, I₂, 4-tert-butylpyridine(4-TBP), GuSCN and 200 nm TiO₂ powders are purchased from Dalian Hepta Chroma SolarTech Co., Ltd. P25 is from Degussa AG, Germany. N719 (cis-bis (isothiocyanato) bis (2, 2’-bipyridyl-4, 4’-dicarboxylato)-ruthenium(II)-bis-tetrabutyl amnonium) is from Solaronix, Switzerland. All purchased chemical reagents used in the study are analytical grade and employed without further purification. Fluorine-doped tin oxide substrate (FTO) 15 ohm/square is purchased from Nippon, Japan and ultrasonically cleaned with detergent water, distilled water and ethanol for 30 min, respectively.

**Fabrication of different TiO₂ nano-crystalline particles.**—Typically, N, La co-doped TiO₂ nano-crystalline particles (NLa/TiO₂) were successfully fabricated by the simple wet method. In detail, the desired amount of La(HNO₃)₃·6H₂O (0.17 g), urea (0.12 g) and 10 mL glacial acetic acid were dissolved in 90 mL deionized water to form solution A at room temperature; 34.03 g tetrabutyltitanate was gradually added into absolute ethanol with constant stirring for 1 h to obtain a pale yellow solution B. Then the solution B was added dropwise to solution A in 60 min with vigorous stirring and after addition the resulting mixture was kept stirring for another 2 h, which was followed by aging for 48 h. The precipitates were centrifuged, washed with water and ethanol 3 times respectively, dried, ground, and calcined at 500°C for 3 h in oven with a heating rate of 5°C/min. Finally, the white powders were obtained.

For comparison, La-doped TiO₂ and N-doped TiO₂ systems were also fabricated according to the same procedure without CO(NH₂)₂ and La(HNO₃)₃·6H₂O, respectively. Meanwhile, La-doped, N-doped and N-La-codoped systems are optimized, in which the optimal doping amount of La and N is 0.4% and 4% (% the mole percent of atoms (La/Ti, N/Ti), respectively. Finally, these optimized samples were designated as La/TiO₂ and N/TiO₂. The pure TiO₂ nano-crystalline particle was also synthesized as the same process without adding dopants.

**Characterization techniques of different TiO₂ nano-crystalline particles.**—FE-SEM (S-4800, Japan Hitachi Ltd) was used to measure the microstructure and size of particles. The crystalline phase of the fabricated samples was identified by X-ray diffraction analysis (XRD, D/MAX-2500, Japan, Rigaku) using Cu Ka radiation (λ = 0.15406 nm), a 40 mA tube current, 40 kV voltage and a 20 range from 10 to 90. The BET specific surface area analysis of the samples was determined by the Brunauer–Emmett–Teller (BET) method (Tristar 3000, Micromeritics, USA). The doping method and the amount of dopants were performed using X-ray photo emission spectroscopy (XPS, PHI-1600, PE, USA) equipped with Mg Ka (1253.6 eV) as the excitation light source with the power at 300.0 W and and the spot size was 0.8 mm².

**Fabrication of different TiO₂ based photoelectrodes at low-temperature and DSSCs assembly.**—Low temperature TiO₂ pastes were fabricated as the following method: 0.8 g of the above fabricated samples, 0.2 g 200 nm TiO₂, 2 g hydrothermal cement (26) and 1 g acetic acid were dispersed in 3 g isopropanol and stirred for 2 h in the ice bath, then NH₄OH was added dropwise and pH was adjusted to about 4.7. The resultant mixture was stirred and treated with ultrasonor method for 2 h, respectively. Finally, the slurry was fabricated after slightly milling, which was applied to FTO substrate with a doctor-blade technique to obtain the photoanode. Afterwards, the photoanode was dried to eliminate the volatile compounds at 120°C for 30 min and the stable low-temperature photoanode was obtained.

Next, the above photoanode was immersed in a dye solution N719 for 18 h to absorb the dye molecules adequately. The DSSCs were assembled to form a sandwich-type cell using the obtained photoanodes, an electrolyte and a Pt counter-electrode. 0.6 M DMPII, 0.03 M I₂, 0.5 M 4-TBP, 0.1 M GuSCN in acetonitrile and valeronitrile (at a volume ratio of 85/15).

**Results and Discussion**

**SEM and TEM analysis.**—The morphology of the as-prepared N, La co-doped TiO₂ samples observed by SEM and TEM images are given in Figs. 1a and 1b. As can be seen from the SEM photograph, many spherical nanoparticles are uniformly distributed and the particle size is about 20 nm. Meanwhile, there are a few agglomeration particles, because those spherical nano-crystallite TiO₂ are connected compactly. Fig. 1b shows that although there are some aggregation of the prepared N, La co-doped TiO₂ sample, most nano-crystallite TiO₂ particles are separated from each other and the dispersity of the particles is good.

**XRD analysis.**—Fig. 2 shows the X-ray diffractogram of pure TiO₂, La/TiO₂, N/TiO₂, N, La/TiO₂ samples in the range of 20–80 (2θ). It can be found that the crystal phase of pure TiO₂-based sample contained both anatase and rutile. However, N-doped TiO₂, La-doped TiO₂ and N, La co-doped TiO₂-based samples do not exhibit any additional phase except for anatase. Thus, we can see that doping N or La can greatly favors the formation of anatase and effectively suppresses the formation of rutile, because the introduction of dopant ions can change the pH of the hydrolysis of TiO₂ sol and promote the formation of anatase phase. Furthermore, it is noteworthy that we do not see the diffraction peak of the dopants in the XRD pattern, which is caused by the small amount of the dopants and their incorporation into TiO₂ lattice or adhesion to the interstitial site. And according to Pauling’s principle, it is not possible for La³⁺ to replace Ti⁴⁺ to enter into the titania lattice because of its larger ion radius (0.108 nm) compared with that of Ti⁴⁺ (0.068 nm). The characteristic peaks of Ti-N and La₂O₃ phases are not observed in the X-ray patterns of doped TiO₂.

**Figure 1.** SEM(a) and TEM(b) photographs of NLa/TiO₂ powder.
samples, which may be due to the reason that N and La have very small doping amounts and cannot form separate phases. These results suggest that La$^{3+}$ may be uniformly distributed in the interstices of titania lattice. The crystalline sizes of the synthesized samples are calculated by using the Scherrer equation $D = \frac{K\lambda}{\beta\cos\theta}$, where $D$ represented the crystal size, $K$ represented the dimensionless shape factor (0.89), $\lambda$ denoted the wavelength of the X-ray irradiation with 0.1541 nm for Cu Ka radiation, $\beta$ expressed the half peak width and $\theta$ was Bragg’s diffraction angle. Those calculated results are collected in the Table II. They are 32.35, 20.14, 19.73 and 18.28 nm for TiO$_2$, La/TiO$_2$, N/TiO$_2$ and N, La/TiO$_2$ powders, respectively. Therefore, the results of XRD image can tell us that doping N, La element can promote the formation of anatase phase and decrease the crystallite sizes of TiO$_2$ samples.

**Laser Raman spectroscopy analysis.**—Laser Raman spectroscopy (LRS) is one of the most effective methods to characterize the near surface structure of inorganic oxides, which is very sensitive to the response of the crystal structure. Fig. 3 is the Laser Raman spectroscopy (LRS) of N, La co-doped TiO$_2$ and N-doped TiO$_2$ samples. As shown in Fig. 3, several Raman bands of the two samples are both observed at about 144, 196, 516, and 638 cm$^{-1}$, which shows that N, La co-doped TiO$_2$ and N-doped TiO$_2$ samples are both anatase phase. At the same time, we can also see that the LRS band of N, La co-doped TiO$_2$ material, in comparison with N-doped TiO$_2$ sample, occurred a slight redshift, and the peak pattern was significantly reduced, which shows that the LRS band of N, La co-doped TiO$_2$ samples is smaller and dispersion is higher. Therefore, the Laser Raman spectroscopy exhibits that not only N, La co-doped TiO$_2$ samples is much smaller, but also the dispersion is better. The results agree well with those obtained from SEM, TEM and XRD images.

**BET analysis.**—Meanwhile, the specific surface area of the four samples was measured by the BET analysis. As shown in Table I, there are 51.04, 106.83, 117.79 and 134.56 m$^2$g$^{-1}$ for pure TiO$_2$, La-doped TiO$_2$, N-doped TiO$_2$ and N, La co-doped TiO$_2$ powders, respectively. N, La co-doped TiO$_2$ sample possesses the biggest specific surface area. The reason is that N, La co-doped TiO$_2$ samples has not only the smallest particle size, but also the best dispersion.

**UV-vis diffuse reflectance spectrum analysis.**—UV-vis diffuse reflectance spectrum of pure TiO$_2$, La/TiO$_2$, N/TiO$_2$, and N, La/TiO$_2$ particles are shown in Fig. 4. Obviously, the light absorption ability of N, La co-doped TiO$_2$ nano-particles is the strongest at the wavelength range from 300 to 650 nm. Especially, at 400–600 nm, the results demonstrate that co-doping with elements of La and N plays a synergistic effect in the enhancement of the light absorption, which is caused by the narrowing bandgaps after doping La and N elements and

---

**Table I. The electro-chemical characteristic of different doping amount of La.**

| Electrodes | Jsc (mA/cm$^2$) | Voc (v) | FF (%) | $\eta$ (%) |
|------------|-----------------|---------|--------|------------|
| La-0       | 7.14            | 0.781   | 71.35  | 3.98       |
| La-1       | 7.45            | 0.7765  | 70.56  | 4.08       |
| La-2       | 8.59            | 0.742   | 70.72  | 4.51       |
| La-3       | 8.03            | 0.782   | 71.45  | 4.47       |

**Table II. Characteristics of powders.**

| Samples | TiO$_2$ | La/TiO$_2$ | N/TiO$_2$ | NLa/TiO$_2$ |
|---------|---------|------------|-----------|-------------|
| Crystallite size/nm | 32.35 | 20.14 | 19.73 | 18.28 |
| Surface area/m$^2$g$^{-1}$ | 51.04 | 106.83 | 117.79 | 134.56 |

---

Figure 2. X-ray diffractogram of the obtain powders.

Figure 3. Laser Raman spectroscopy (LRS) of N, La co-doped TiO$_2$ and N-doped TiO$_2$ samples.

Figure 4. UV-vis diffuse reflectance spectrum of samples TiO$_2$, La/ TiO$_2$, N/TiO$_2$, and NLa/TiO$_2$ particles.
increasing light absorption in the visible light region. Generally, TiO$_2$ is a material with a large bandgap and only absorbs ultraviolet light, however, the ultraviolet light only accounts for 2–4% of the solar light that can reach the earth’s surface, while visible light has accounted for 48%. Therefore, narrow bandgaps can greatly increase the light harvesting yield of the solar light that can reach the earth’s surface. To confirm that the bandgaps are narrowed after co-doping, the bandgap energy of the samples was calculated through the Kubelka-Munk equation, which are 3.16, 3.01, 2.90 and 2.83 eV for pure TiO$_2$, La-TiO$_2$, N-TiO$_2$, and N, La co-doped TiO$_2$ powders, respectively. It is true that the highest light absorption of N, La co-doped TiO$_2$ sample is due to the smallest bandgap energy. Namely, above the valence band for the substitutional nitrogen and below the conduction band for La$^{3+}$ doping can form a dopant level, which could decrease the bandgap of TiO$_2$. The doping of La$^{3+}$ will cause lattice deformation and form vacancies, which will probably result in an impurity state of titania. The existing of impurity state can narrow the bandgap and improves the light absorption.

**XPS analysis.**—X-ray photoelectron spectroscopy (XPS) is performed to determine the surface component and chemical state of the samples. Fig. 5a is the full scanned spectra of N, La co-doped TiO$_2$ powder in the range of 0–1100 eV. Obviously, N and La element are introduced successfully into the sample. It is true that the highest light absorption of N, La co-doped TiO$_2$ sample is due to the smallest bandgap energy. Namely, above the valence band for the substitutional nitrogen and below the conduction band for La$^{3+}$ doping can form a dopant level, which could decrease the bandgap of TiO$_2$. The doping of La$^{3+}$ will cause lattice deformation and form vacancies, which will probably result in an impurity state of titania. The existing of impurity state can narrow the bandgap and improves the light absorption.

**Photovoltaic performance studies.**—Fig. 6 shows the photovoltaic performances of the current–voltage characteristics and the corresponding photovoltaic characteristics such as the short circuit current ($I_{sc}$), open-circuit photovoltage ($V_{oc}$), fill factor (FF) and photoelectric conversion efficiency ($\eta$) are summarized in Table III. It can be seen
that N, La co-doped TiO2-based DSSCs has the maximum photoelectric conversion efficiency 5.33%, while the photoelectric conversion efficiency of N-doped and La-doped TiO2 cells are 4.72% and 4.58%, respectively. And the pure TiO2-based cell is only 4.02%. Compared with the pure TiO2-based DSSC, La-doped TiO2-based cell and N-doped TiO2-based cell, the photoelectric conversion efficiency of the co-doped TiO2-based DSSC was increased by 32.6%, 16.4% and 12.9%, respectively. Obviously, higher $J_sc$ (10.52 mA/cm$^2$) is found for co-doped DSSC when compared with the N-doped (9.33%), La-doped (8.88%) and the pure TiO2-based DSSC (7.92% mA$^{-1}$cm$^{-2}$), a pronounced enhancement of $J_sc$ (12.8%, 18.5%, 32.8%) is observed for the co-doped solar cell over the DSSCs using the N-doped TiO2 electrodes, La-doped TiO2 electrodes and pure-TiO2 electrodes, respectively. Simultaneously, it is noteworthy that both $V_oc$ and FF of the co-doped TiO2-based solar cell are decreased, this is ascribed to forming Ti-O-N, Ti-O-N-O and Ti-O-La bonds after doping N and La elements into TiO2 lattice, which increased the disorder of the lattice structure and resulted in the trap states. Therefore, the enhanced performance mainly depended on the Jsc changes.

In order to find out the reasons for the increase of the short circuit current, the amount of dye adsorption of the four types of cells are measured and shown in Fig. 7. Meanwhile, the values are collected in Table III, N, La co-doped TiO2-based cell absorbs the most dye $(7.11 \times 10^{-7}$ mol•cm$^{-2}$), while the pure TiO2-based cell absorbs the least $(3.21 \times 10^{-7}$ mol•cm$^{-2}$). The results are ascribed to the crystalline size of the samples. The size of N, La co-doped TiO2 sample is the smallest, while that of pure TiO2 is the biggest. The smaller crystalline size, the larger the surface areas, and the more dye loading amount. N, La co-doped TiO2-based DSSCs has greatest amount of dye molecules absorbed, which led to the highest short circuit current.

The charge transport and the electrons lifetime were investigated by EIS analysis to determine another reason for the enhanced Jsc value when treated with N, La co-doping, La-doping and N-doping, respectively. Typically, the EIS Nyquist plot of DSSCs has three semicircles with increasing frequency. The three semicircles correspond to the diffusion resistance within the electrolyte at low frequency, electron transport resistance at the oxide/electrolyte interface at middle frequency, and the resistance of redox reaction at the platinum counter electrode at high frequency. However, in our survey, only two semicircles can be observed, and the resistance of diffusion within the electrolyte at low frequency do not show up, which is explained by the limited frequency range of our instrument (from 1 Hz to 1000 Hz under the same conditions with $J-V$ measurement and the open circuit voltage is set as the open applied bias voltage); however, the diffusion process is normally observed over the frequency range 0.01 Hz and 0.1 Hz. Fig. 8a is the Nyquist image of the four cells. The detailed EIS parameters are as shown in Table IV. Rs represents the external circuit resistance, $R_2$ represents the resistance of redox reaction at the platinum counter electrode, $R_2$ represents the resistance of electron transport at the oxide/electrolyte interface. From Table IV, we can see that the values of Rs, $R_2$ and $R_3$ all decrease after doping N, La element, because the sizes become smaller after doping, thus TiO2 particles and FTO substrate become closer, which increase the inter-connection between the TiO2 particles or contact with FTO substrate. $R_3$ has a great influence on DSSCs for different photoanodes. From Table IV, it can be seen that $R_3$ value of the N, La co-doped TiO2-based solar cell is the smallest, which means that N, La co-doped TiO2-based cell has the smallest electron transport resistance, indicating that the electron transport of N, La co-doped TiO2-based DSSCs is faster than that of others. Therefore, N, La co-doped TiO2-based cell has the highest Jsc. Fig. 8b shows the Bode plots of the four type DSSCs, the first peak at low frequency stands for the lifetime of electrons at the TiO2/dye/electrolyte interface, and the value of the electron lifetime are also summarized in Table III. Obviously, N, La co-doped TiO2-based DSSC has the longest electron lifetime (19.29 ms), while the pure TiO2-based DSSC has the shortest one (6.10 ms), which also shows that N, La co-doped TiO2-based solar cell has higher Jsc.

---

**Table III.** Performance characteristics of the low-temperature dye-sensitized solar cell.

| Electodes   | Jsc (mA/cm$^2$) | Voc (v) | FF (%) | $\eta$ (%) | Amount of dye / mol•cm$^{-2}$•10$^{-7}$ |
|-------------|-----------------|--------|--------|------------|---------------------------------------|
| TiO2        | 7.92            | 0.74   | 70.11  | 4.02       | 3.21                                  |
| La/TiO2     | 8.8766          | 0.7307 | 70.68  | 4.58       | 5.14                                  |
| N/TiO2      | 9.33            | 0.736  | 68.67  | 4.72       | 6.23                                  |
| NLa/TiO2    | 10.518          | 0.7277 | 69.582 | 5.33       | 7.11                                  |
temperature DSSCs. The photoelectric conversion efficiency reached LEDs, which led to high photo current density. By narrowing bandgaps and increasing visible light absorption, which resulted in an increased light-harvesting was realized in doped TiO₂-based cell, the performance mainly depended on the improvement of Jₛ, which is attributed to the increase of the dye absorption amount, electron lifetimes, and the decrease of the charge transport resistance after doping non-metal element N and rare-earth metal element La into TiO₂ photoanode. Simultaneously, increasing the light-harvesting was realized by narrowing bandgaps and increasing visible light absorption, which led to high photo current density.

Conclusions

We synthesized N, La co-doped TiO₂ samples fabricated for low-temperature DSSCs. The photoelectric conversion efficiency reached 5.33%, with a Vₚ of 728 mV, Jₛ of 10.518 mA cm⁻², and FF of 69.58%. When compared with that of pure TiO₂-based, La and N-doped TiO₂-based cell, the η of N, La co-doped TiO₂-based cell increased by 32.6%, 16.4% and 12.9%, respectively. The enhanced performance mainly depended on the improvement of Jₛ, which is attributed to the increase of the dye absorption amount, electron lifetimes, and the decrease of the charge transport resistance after doping non-metal element N and rare-earth metal element La into TiO₂ photoanode. Simultaneously, increasing the light-harvesting was realized by narrowing bandgaps and increasing visible light absorption, which led to high photo current density.

Acknowledgments

This work is supported by Natural Science Foundation of China (no. 21076147) and China International Science and Technology Project (no. 2012DFG41980).

References

1. L. Y. Han, A. Islam, H. Chen, C. Malapaka, B. Chiranjeevi, S. F. Zhang, X. D. Yang, and M. Yanagida, *Energy Environ. Sci.*, 5, 6057 (2012).
2. Y. M. Xiao, J. H. Wu, J. M. Lin, M. L. Huang, L. Q. Fan, Z. Lan, G. Y. Han, and S. D. Li, *Electrochim. Acta.*, 117, 1 (2014).
3. Y. M. Xiao, J. H. Wu, G. T. Yue, J. M. Lin, M. L. Huang, L. Q. Fan, and Z. Lan, *Electrochim. Acta.*, 58, 621 (2011).
4. Y. M. Xiao, J. H. Wu, G. T. Yue, J. M. Lin, M. L. Huang, L. Q. Fan, and Z. Lan, *J. Power Sources.*, 208, 197 (2012).
5. J. Wu, Y. Xiao, G. Yue, Q. Tang, J. Lin, M. Huang, Y. Huang, L. Fan, Z. Lan, S. Yin, and T. Sato, *Adv. Mater.*, 24, 1884 (2012).
6. M. Hiraishi, L. De Marco, G. De Pellegrino, G. G. Condorelli, R. Giannuzzi, R. Scarfelli, M. Manca, C. Spinella, G. Gigli, A. La Magna, C. Spinella, G. Gigli, and A. La Magna, *ACS Appl. Mater. Interfaces.*, 6, 6425 (2014).
7. M. Dür, A. Schmid, M. Obersaier, S. Rosselli, A. Yasuda, and G. Nelles, *Nature Chem.*, 4, 607 (2005).
8. T. Yamaguchi, N. Tobe, D. Matsumoto, T. Nagai, and H. Arakawa, *Sol. Energy Mat. Sol. C.*, 94, 812 (2010).
9. D. S. Zhang, T. Yoshida, K. Furuta, and H. Minoura, *J. Photochem Photobiol A: Chem.*, 164, 159 (2004).
10. C. Y. Li, Y. Lin, X. P. Li, Z. P. Wang, Y. T. Ma, X. W. Zhou, S. J. Feng, and X. R. Xiao, *Chinese Sci. Bull.*, 50, 1449 (2005).
11. F. Pichot, J. R. Pitts, and B. A. Gregg, *Langmuir.*, 16, 5626 (2000).
12. D. Zhang, T. Yoshida, T. Oekermann, K. Furuta, and H. Minoura, *Adv. Funct. Mater.*, 12, 1228 (2006).
13. S. Uchida, M. Tomiha, H. Takizawa, and M. Kawaraya, *J. Phys.* Chem. C., 122, 93 (2013).
14. R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, and Y. Taga, *J. Phys.* Chem. C., 122, 4369 (2011).
15. F. Zhang, C. C. Yu, S. W. Yan, J. T. Pan, B. Chi, J. Fu, and L. Jian, *J. Am. Ceram. Soc.*, 95, 1372 (2012).
16. W. Guo, Y. H. Shen, and T. L. Ma, *Electrochim. Acta.*, 56, 4611 (2011).
17. C. W. Hsu, P. Chen, and J. M. Ting, *J. Electrochem. Soc.*, 160, 160 (2013).
18. Y. Y. Chen, B. Zhang, and Y. Q. Feng, *Res Chem. Intermed.*, 36, 2215 (2010).
19. W. Qin, S. T. Lu, X. H. Wu, and S. Wang, *Int. J. Electrochem. Sci.*, 8, 7984 (2013).
20. M. N. An`amt, S. Radiman, N. M. Huang, M. A. Yarmo, N. P. Ariyanto, H. N. Lim, and M. R. Muhamad, *Ceram. Int.*, 36, 2215 (2010).
21. M. N. An`amt, S. Radiman, N. M. Huang, M. A. Yarmo, N. P. Ariyanto, H. N. Lim, and M. R. Muhamad, *Ceram. Int.*, 36, 2215 (2010).
22. Q. Wang, J. F. Liang, R H Zhang, Q. Li, and J. F. Dai, *Chin. Phys. B.*, 22, 057801 (2013).
23. S. Han, H. Kobayashi, K. Ikarashi, N. Saito, H. Nishiyama, and Y. Inoue, *J. Phys. Chem. B.*, 108, 4369 (2004).
24. T. J. Trentler, T. E. Denier, and J. F. Bertone, *J. Am. Chem. Soc.*, 121, 1613 (1999).
25. X. L. Zhang, Z. A. Wang, Z. Luo, and X. Liu, *Asian J. Chem.*, 23, 2343 (2011).
26. W. Guo, Y. H. Shen, and T. L. Ma, *Electrochim. Acta.*, 56, 4611 (2011).
27. J. Parker and R. Siegel, *Appl. Phys. Lett.*, 57, 943 (1990).
28. T. J. Trentler, T. E. Denier, and J. F. Bertone, *J. Am. Chem. Soc.*, 121, 1613 (1999).
29. F. Spadavecchia, C. Cappelletti, S. Ardizzone, C. L. Bianchi, C. Sappelli, C. Oliva, F. Scardi, M. Leoni, and P. Fermo, *Appl. Catal., B: Environ.*, 96, 314 (2010).
30. X. H Xu, Y. Tian, and J F Wu, *Wuhan Univ. Technol.,* 30, 543 (2008). (in Chinese).
31. Y. Cong, B. Z. Tian, and J. L. Zhang, *Appl. Catal., B: Environ.*, 101, 376 (2011).
32. X. W. Cheng, J. Y. Yu, Z. P. Xing, and J. F. Wan, *Energy Procedia.*, 16, 598 (2012).
33. J. W. Liu, R. Han, Y. Zhao, H. T. Wang, W. J. Lu, T. F. Yu, and Y. X. Zhang, *J. Phys. Chem. C.*, 115, 4517 (2011).
34. H. Wang, H. Y. Li, J. S. Wang, J. S. Wu, D. S. Li, M. Liu, and P. L. Su, *Electrochim. Acta.*, 137, 744 (2014).
35. L. Q. Jing, X. J. Sun, B. F. Xin, B. Q. Wang, W. M. Cai, and H. G. Fu, *J. Solid State Chem.*, 177, 3375 (2004).
36. Ch. P. Hsu, K. M. Lee, T. W. Huang, C. H. Lin, C. L. Lee, L. P. Wang, S. Y. Tsai, and K. Ch. Ho, *Electrochim. Acta.*, 53, 7514 (2008).

Table IV. EIS Parameters of the N-doped TiO₂ and undoped TiO₂ DSSCs.

| Samples     | R(Int)(Ω) | R(∥)(Ω) | R(∥)(Ω) | F(Hz) | t(μs) |
|-------------|-----------|---------|---------|-------|-------|
| TiO₂        | 4.45      | 3.651   | 7.589   | 26.1  | 6.097 |
| La/TiO₂     | 3.97      | 3.54    | 7.23    | 12.1  | 13.15 |
| N/TiO₂      | 3.843     | 2.923   | 6.858   | 10    | 15.92 |
| NLa/TiO₂    | 3.914     | 2.857   | 6.506   | 8.25  | 19.29 |

Figure 8. Nyquist(a) and Bode(b) plots of the samples TiO₂-based DSSC.