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ARTICLE

Preparation and Property of La, Nd, Bi Co-doped TiO_2 Electrochromic Film

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Abstract: To improve optical property and coloration effect, La, Nd and Bi co-doped TiO_2 films were synthesized via a sol-gel method, using butyl titanate as precursor on the surface of ITO glass substrate. Structures and surface optical electrochromic properties of the as-prepared films were examined with XRD, UV-vis and electrochemical workstation. The results show that anatase TiO_2 forms from TiO_2 dry gels after heat treatment at 400, 500, and 600 ℃, and the higher the heat treatment temperature, the more complete the crystal development. La, Nd and Bi doping increases the disorder of the TiO_2 octahedron, resulting in an increase of the amorphization degree. TiO_2 films prepared with volume fraction 12% tetrabutyl titanate exhibit excellent electrochromic properties. TiO_2 films heat-treated at 500 ℃ show the best electrochromic properties. TiO_2 films singly doped with 8% La, 18% Nd, and 6% Bi (molar fraction) possess excellent electrochromic properties, and single doping effect is in the order of 6% Bi< 8% La<18% Nd. La-Nd-Bi co-doped TiO_2 is anatase type with a very high amorphization degree, and the best cyclic voltammetry and the highest amorphization degree can be achieved when the molar ratio of La:Nd:Bi is 4:10:2.

Key words: electrochromism; sol-gel; La-Nd-Bi co-doped TiO_2 film; cyclic voltammetry; coloration efficiency

Electrochromism refers to the reversible color change of material's optical properties (reflectivity, transmittance, absorptivity, stability, etc.) under the action of electric field. Electrochromism exhibits reversible changes in color and transparency in appearance[1-3]. Electrochromic materials can be classified into three types from the state of matter: the commonly used solid film type, the solid and liquid interconversion precipitation type and the solution non-precipitation type. Electrochromic materials can be divided into inorganic materials and organic materials[4-6]. At present, many kinds of preparation methods of electrochromic films have been used, and the electrochromic films obtained by different preparation methods differ to some extent in structure and composition, leading to great differences in the electrochromic properties of the films. The preparation methods of the electrochromic film mainly include sol-gel, vacuum sputtering and vacuum evaporation. Among them, the sol-gel method is suitable for large-area coatings and has a simple process. It is one of the most promising methods for preparing film materials[7,8].

When the titanium dioxide film is under low voltage, its color is blue; the bleached state is colorless and transparent, and has no additional color effect on transmission light, which is suitable for the preparation of building intelligent film material, namely, the "intelligent window". However, the TiO_2 film has the disadvantages of long reaction time and poor ion storage capacity. The discoloration effect of the device will fade quickly and it is difficult to process a large area. Therefore, it is difficult to prepare all solid-state electrochromic devices. At present, there are very few electrochromic devices in practice, and most of them are still in the laboratory research stage. It is a hot topic to study and prepare electrochromic devices with cycles more than 105~106, fast response time, large area and all solid state. It has been found that preparation of all solid ionic conductive materials with excellent properties is the key to increase the cycle times. Sol-gel method is a common method for preparing large-area films. Therefore, efforts should be made in basic research on

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material structure, properties, material synthesis, electrochromic mechanism, and film formation factors. Rare earth doping modification has obtained the most critical application in TiO_2 film doping modification technology[9,10].

In order to further improve the electrochromic properties of TiO_2 films, many metal ion doping techniques have been reported, such as Ce^{3+}, Sm^{3+}, V^{5+}, etc[11]. And to some extent, the performance of TiO_2 film is improved, but La^{3+} doped TiO_2 still stays in its photocatalytic performance research[12]. Few reports have been reported on the electrochemical properties of TiO_2 films doped by La, Nd and Bi. In this work, TiO_2 precursors were prepared by sol-gel method[13,14] with tetrabutyl titanate to prepare a La, Nd and Bi doped TiO_2 film, and its structure and electrochromic properties were systematically characterized and analyzed. The color change mechanism was studied in detail.

1 Experiment

1.1 Preparation of TiO_2 electrochromic film by doping metal ion modification

First, a certain amount of tetrabutyl titanate ($Ti(OC_4H_9)_4$), acetic acid and anhydrous ethanol were put into the beaker. After 1 h of intense stirring, homogeneous pale yellow transparent liquid precursor A could be obtained. Then a certain amount of transition metal oxide (lanthanum oxide: La_2O_3), transition metal salts ($Nd(NO_3)_3$, $Bi(NO_3)_3$ $5H_2O$), nitric acid, deionized water and anhydrous ethanol were put into the beaker. After intense stirring for 30 min, homogeneous and transparent precursor solution B could be obtained.

Then, the A and B liquids were mixed and stirred for 1 h, and aged for 12 h to obtain precursor sols with different mass fractions of transition metal ion doped TiO_2. TiO_2 films doped with transition metal ions were prepared on ITO conductive glass substrate by dip extraction. The ITO conductive glass was immersed in a mixed solution of acetone and ethanol for 30 min, ultrasonically cleaned for 10 min, completely dried, and then impregnated into the aged sol and pulled repeatedly at a constant rate of 3 mm/s. Finally, the dried substrate was placed in a box-type resistance furnace; set the heating rate of 0.5 ℃/min until the temperature reached 300 ℃, and then set the heating rate to 3 ℃/min until the temperature reached 500 ℃, and then kept it for 2 h to obtain the transition metal ions doped TiO_2 film.

1.2 Characterization

Cyclic voltammetry and optical properties of La^{3+} doped TiO_2 films were analyzed using CHI660E electrochemical workstation (trielectrode method, using a standard 1 mol/L $LiClO_4$+PC electrolyte solution at a scan rate of 0.05 mV/s) and UV spectrophotometer (UV-Vis). The composition of TiO_2 xerogel powder was tested using X-ray diffractometer (χ'Pert PRO, Cu Kα radiation, voltage 40 kV, current 40 mA, wavelength 0.154 05 nm).

2 Results and Discussion

2.1 Electrochromic properties of TiO_2 films

2.1.1 Effect of tetrabutyl titanate content on volt-ampere characteristics of TiO_2 films

Fig.1 shows the cyclic voltammetry (CV) curves of TiO_2 films prepared with different tetrabutyl titanate contents, in which Ti 1, Ti 2 and Ti 3 correspond to the samples with tetrabutyl titanate of 10vol%, 12vol% and 14vol%, respectively. Heat treatment temperature is 500 ℃ and the cycle is 25 times. The voltage in the cyclic voltammetry (CV) curves gradually decreases from 2 V to –2 V, indicating that the current density gradually increases. Li^+ and e^- are implanted into the TiO_2 film. The film is shown in blue and appears as a coloring process accompanied by an obvious cathode peak. When voltage back-sweep is set, corresponding to the extraction of Li^+ and e^- from the TiO_2 film, the blue film gradually fades, that is, the bleaching process, accompanied by weak anode peak. The CV curves between –0.4~1.8 V are straight lines, that is, the current value is close to zero, which may be caused by the excessive resistivity of the film. 25 cyclic scanning test were conducted. The test results show that the cyclic voltammetry curves are basically coincident, indicating that the TiO_2 film electrochromism has excellent cycle stability[15].

The cathode peak current density value of Ti 2 (12vol% tetrabutyl titanate) is the largest, indicates the electrochemic activity of the Ti 2 film is the best.

2.1.2 Effect of calcination temperature on volt-ampere characteristic of TiO_2 films

Fig.2 is the cyclic voltammetry (CV) curve of TiO_2 films heat treated at different temperatures, in which the volume fraction of tetrabutyl titanate is 12% and the cycle is 25 times. Fig.2 shows that the response current of the film with heat treatment temperature of 400 and 500 ℃ is large; when the heat treatment temperature is 600 ℃, the cyclic voltammetry characteristics of the film is poor, and the corresponding anodic oxidation peak and cathode reduction peak significantly

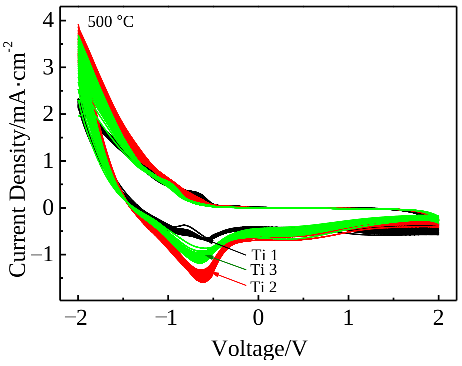

Fig.1 Cyclic voltammetry curves of TiO_2 films prepared with different tetrabutyl titanate contents

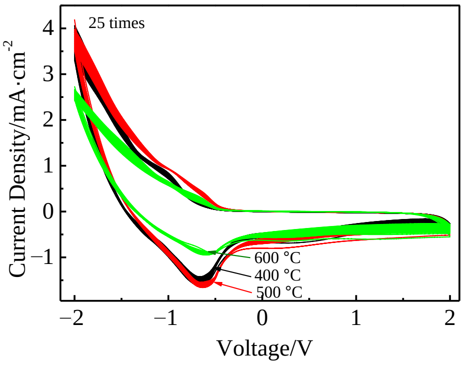

Fig.2 Cyclic voltammetry curves of TiO_2 films heat-treated at different temperatures

decrease. At the same time, as the heat treatment temperature increases, the position of the cathode injection peak of the corresponding cyclic voltammetry curve of the film also moves in the positive direction. The anodic oxidation peak of the TiO_2 film heat treated at 400 ℃ is higher than at 500, 600 ℃. Through comparative analysis of three kinds of cyclic volt-ampere curve of TiO_2 film with different heat treatment temperatures, it can be found that the film with heat treatment temperature of 500 ℃ has a large redox peak surrounding area, high peak current value, good stability, and excellent electrochemical performance.

Fig.3a, 3b and 3c correspond to cyclic voltammetry curves of TiO_2 films with different scanning rates at 400, 500 and 600 ℃, respectively. As can be seen from the figure, increasing the scanning rate of voltage also increases the response current, because electrochromism is a diffusion process. When the scanning rate is low, electrochromism tends to stabilize. A lower scan rate provides sufficient time for the Li^+ ions to diffuse, complete the redox reaction, and form a reversible photochromic substance. At the same time, the current response lags, and the corresponding peak current voltage also decreases. This is because a lower scanning rate leads to a significant hysteresis effect on the response current and voltage. The delayed peak current potential and the redox peak potential deviate to positive/negative potential to a certain extent, respectively. However, the slow scanning rate will cause ion implantation to be irreversible, so the scan rate is also a key factor in studying the electrochemical performance of the film[16].

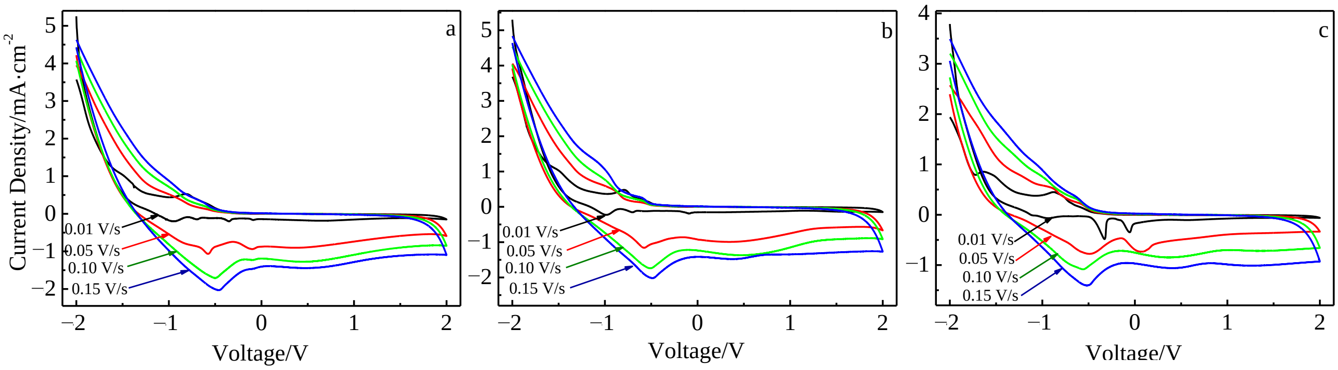

Fig.3 Cyclic voltammetry curves of TiO_2 films heat-treated at different scanning rates and different temperatures: (a) 400 ℃, (b) 500 ℃, and (c) 600 ℃

2.1.3 Coloring efficiency of TiO_2 films

Coloring efficiency CE(λ) is an important parameter for measuring the electrochromic properties of materials, and its definition can be seen in Eq.(1) and Eq.(2):

$$\mathrm{CE}(\lambda)=\Delta\mathrm{OD}(\lambda)/Q \qquad (1)$$

$$\Delta\mathrm{OD}(\lambda)=\lg(T_b/T_c) \qquad (2)$$

where ΔOD(λ) represents the change in optical density of the material or device at the wavelength λ in the fading state; T_b and T_c are the transmittances of the bleached and colored states at the wavelength λ, respectively; Q represents the injection or extraction of the charge per unit area. Fig.4 is a coloring efficiency spectrum of titanium dioxide film with 12% tetrabutyl titanate at different temperatures. It can be seen that when the heat treatment temperatures is lower, the coloring efficiency of the film is higher, up to 10 cm^2/C; when the wavenumber is 200~800 nm, the coloring efficiency of TiO_2

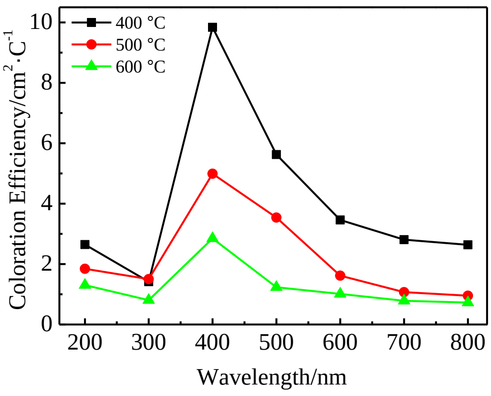

Fig.4 Coloration efficiency (CE) of TiO_2 film with 12% tetrabutyl titanate at different temperatures

film will decrease first, then rise and fall. When the wavelength is 400 nm, the coloring efficiency value of TiO_2 film is the highest. The XRD analysis of TiO_2 films treated at different temperatures shows that the crystal structure of the films does not change after heat treatment at 400, 500 and 600 ℃. Fig.5 shows the XRD patterns of TiO_2 films heat treated at different temperatures. The analysis results in Fig.5 show that the lower the crystallization temperature of the amorphous phase, the higher the degree of amorphous phase, and the trend of loose bonding is presented, which makes the input and extraction of ions easier, and the corresponding electrochromic performance is better. The analysis results of the discoloration performance are consistent.

2.1.4 Spectral performance of TiO_2 film

The transmittance spectra of colored and bleached TiO_2 films prepared with different butyl titanate contents and heat treated at different temperatures are shown in Fig.6 and 7, respectively. The transmittance analysis of the TiO_2 film heat treated at different temperatures shows that the transmittance of the titanium dioxide film in the visible light range is about 80%, but the transmittance in the ultraviolet region is very low, close to zero. In addition, both Fig.6 and 7 show that the zero transmittance of the film after coloration is extended from the ultraviolet region to 400 nm of visible light, indicating that ion implantation contributes to absorption of waves less than or equal to 400 nm. It is found in Fig.6 that the transmittance in the colored state is much lower than that in the bleached state, which further demonstrates the superiority of the electrochromic performance of the TiO_2 film, and the transmittance does not increase with the increase of the content of butyl titanate, indicating that the butyl acrylate content has little effect on the transmission rate. It can be seen from Fig.7 that the transmittance in the colored state is much lower than that in the bleached TiO_2 film, and the difference in the coloration/bleaching state of the TiO_2 film after heat treatment at 500 ℃ is the most obvious, which does not conform to the analysis result of Fig.6, Therefore, the transmittance is not the only indicator for measuring the coloring efficiency of the film. The influence factors of the coloring efficiency of the

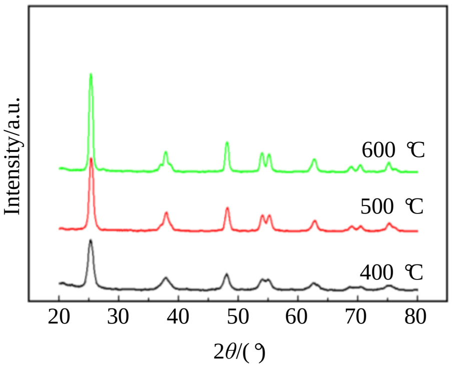

Fig.5 XRD patterns of TiO_2 films heat-treated at different temperatures

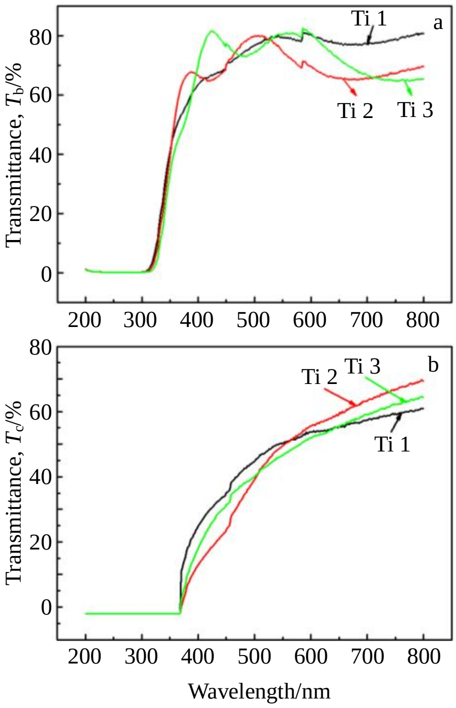

Fig.6 Transmittances of TiO_2 films prepared with different contents of tetrabutyl titanate: (a) T_b and (b) T_c

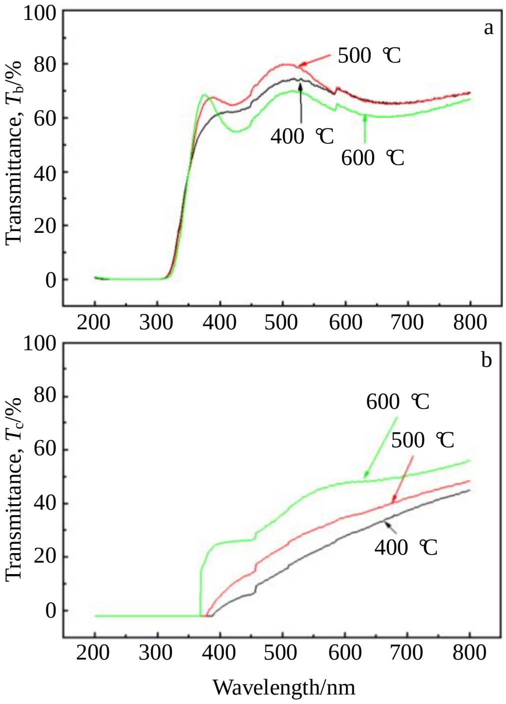

Fig.7 Transmittances of TiO_2 films heat-treated at different temperatures: (a) T_b and (b) T_c

film also include the storage capacity of the ions.

2.2 Modification of TiO_2 electrochromic films doped with lanthanum, neodymium and bismuth

According to ΔT ($\Delta T=(T_b-T_c)/T_b\times 100\%$)value size order for Bi<La<Nd and different molar doping amounts of La, Nd, Bi doped TiO_2 film transmittance, single doping experiment design the La, Nd, Bi molar doping amount is 6% Bi, 8% La and 18% Nd. The results are shown in Fig.8.

Fig.8 is cyclic voltammetry curves and ΔT curves of La, Nd and Bi singly doped TiO_2 films. From Fig.8a, the current density of the cyclic voltammetry curves of La, Nd and Bi single-doped TiO_2 films increases gradually as the voltage decreases from 2 V to –2 V. It indicates that Li^+ and e^- are implanted into the TiO_2 film. The blue color of the film is a coloring process accompanied by several cathode peaks. When the voltage increases from –2 V to 2 V, the current density curve gradually decreases. When Li^+ and e^- are extracted from the TiO_2 film, the blue film gradually fades, which is the bleaching process, accompanied by a weaker anode peak. In addition, when the voltage increases from 0.5 V to 2 V, the volt-ampere curve is a straight line, the current value is almost zero, and the current strength between the electrodes hardly changes. This may be the reason for the high resistivity of the film. Fig.8a shows that La, Nd, Bi doping can improve the electrochemical performance of TiO_2 film to various degrees. The order of improvement of electrochemical performance is Bi<La<Nd. It is also found that the electrochemical properties of La and Bi doped TiO_2 film are not obvious, and only the adhesion between the sol and the ITO glass is improved. Nd doping can improve the electrochemical performance of TiO_2 film, but the adhesion between sol and ITO glass is poor, and the film tends to peel off. Fig.8b shows that the ΔT curve of the TiO_2 film without La, Nd and Bi doping decreases in the wavelength range of 400~800 nm. It can be concluded that the light absorption of the colored TiO_2 film in the visible light range is related to the wavelength, and the shorter the wavelength, the easier it is for TiO_2 to absorb, resulting in a larger ΔT, a decrease in transmittance, and the order of ΔT values after doping is Bi<La<Nd, consistent with the voltammetry curve analysis results of the film.

Fig.9 is a ΔT curve of 6% La and 6% Bi doped TiO_2 film. It can be seen that the La doping effect is better than the Bi doping effect under the same doping amount.

Fig.10 is XRD patterns of La, Nd, and Bi co-doped TiO_2 film (preparation temperature is 500 ℃). It can be seen that characteristic peaks appear at $2\theta=25.45°$, corresponding to the (101) crystal plane of TiO_2 anatase phase (PDF#99-0008). However, the other characteristic peaks corresponding to the TiO_2 anatase phase seem to be dispersed, indicating that the co-doping of La, Nd and Bi seriously damages the crystal structure of the TiO_2 anatase phase. When the doping molar ratio is La:Nd:Bi=4:10:2, the XRD characteristic peak value of the doped sample is the minimum, and the amorphous degree of the corresponding sample is the highest. The higher the amorphous degree of TiO_2 crystal, the looser the combination, which is more conducive to the input and extraction of ions. The electrochromic performance of doped TiO_2 film is also better. However, the doping ions enter the interior of TiO_2 lattice, resulting in crystal defects. The higher the co-doping amount of La, Nd and Bi, the higher the amorphous degree of the crystal, and the better the electrochromic performance of the crystal. In this study, when the doping molar ratio La:Nd:Bi=4:10:2, the degree of doping

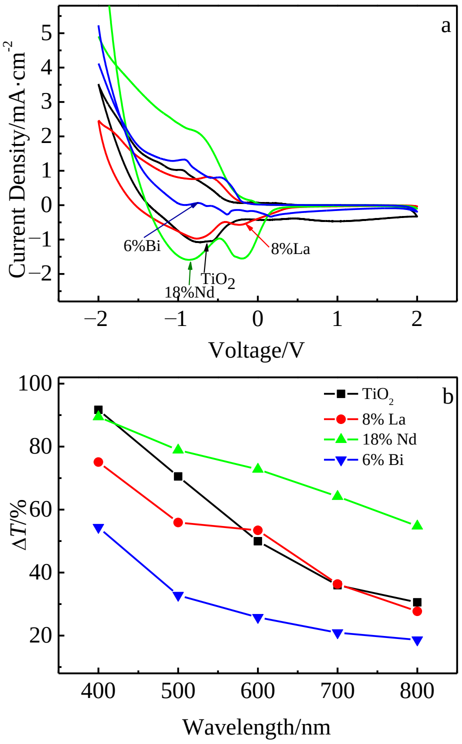

Fig.8 CV (a) and ΔT (b) curves of TiO_2 films singly doped with molar fraction of 8% La, 18% Nd and 6% Bi

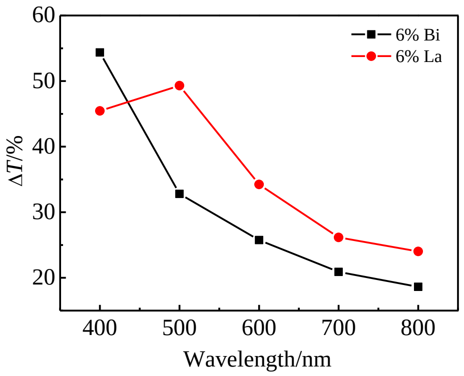

Fig.9 ΔT curves of TiO_2 films doped with molar fraction of 6% La and 6% Bi

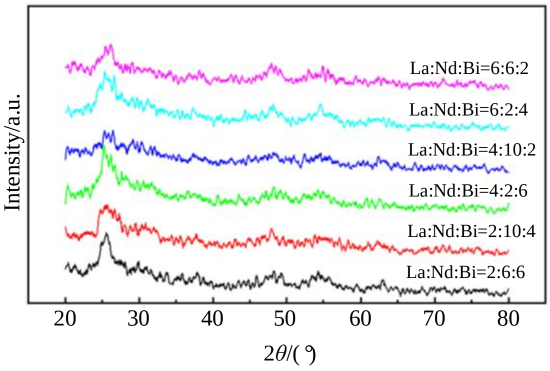

Fig.10 XRD patterns of La, Nd and Bi co-doped TiO_2 films with different molar ratios

TiO_2 amorphous phase is the highest.

Fig.11 is cyclic voltammetry curves of La, Nd, Bi co- doped TiO_2 film, and the inset is partially enlarged cyclic voltammetry curve. It can be seen from Fig.11 that after scanning the La, Nd, Bi co-doped TiO_2 film at a scanning rate of 0.05 mV/s in a 1 mol/L $LiClO_4$+ PC electrolyte for one cycle, a clear cathode reduction peak appears in the cyclic voltammetry curve. When the voltage changes from 2 V to –2 V, the cyclic voltammetry curves of La, Nd and Bi co-doped TiO_2 films show a gradual increase of current density. When scanning from 0.5 V to 2 V, the corresponding *I-V* curve is a straight line, and the current value is almost zero. When the voltage is swept from –2 V to 2 V, the current density curve gradually decreases. The inset shows that when La:Nd:Bi= 4:10:2, the cathode reduction peak of the corresponding film is large and sharp, and it can be seen from the analysis of Fig.10 that when La:Nd:Bi=4:10:2, the degree of amorphous phase of the corresponding film is the highest, indicating that the cyclic voltammetry of the film is also affected by the crystal structure and the degree of amorphous phase. After the introduction of ions, the TiO_2 octahedral void structure changes from a quadrilateral to a larger triangular, pentagonal and hexagonal tunnel. This structure facilitates the rapid transmission of small metal ions, thus improving the cyclic voltammetry characteristics of films. La, Nd and Bi co-doped TiO_2 films are colored transparent blue and bleached light blue transparent. The La, Nd, Bi co-doped TiO_2 film is colored under an applied voltage of –2 V, and bleached under an applied voltage +2 V.

Fig.12b shows that when the film is in the colored state, its visible light transmittance is between 40% and 60%, and the film has the lowest transmittance when La:Nd:Bi=4:10:2, indicating that the La, Nd, Bi co-doped TiO_2 film has excellent optical control performance in the visible range. Fig.12c is ΔT curves of lanthanum, neodymium and bismuth co-doped TiO_2 film. It can be seen that the increase or decrease of ΔT curves are slightly different when the doping amounts of lanthanum, neodymium and bismuth are different. When the doping molar ratio of La:Nd:Bi is 2:6:6 and 2:10:4, the corresponding film ΔT curves first drop, then increase and then decrease again. When the doping molar ratio of La:Nd:Bi are 6:2:4 and 4:2:6, the ΔT curve of the corresponding co-doped TiO_2 film first decreases and then increases. When La:Nd:Bi is 4:10:2 and 6:6:2, the ΔT curve of the co-doped TiO_2 film shows a monotonous decrease. Comprehensive comparative

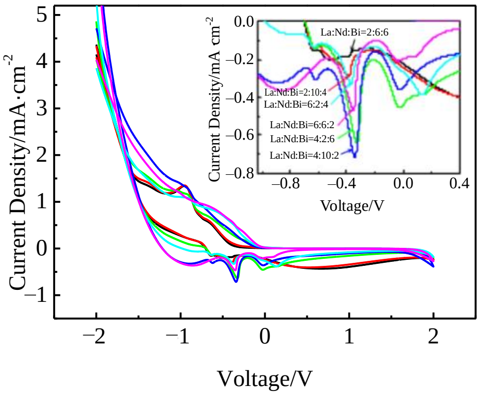

Fig.11 Voltammetry characteristic curves of La, Nd and Bi co-doped TiO_2 films with different molar ratios

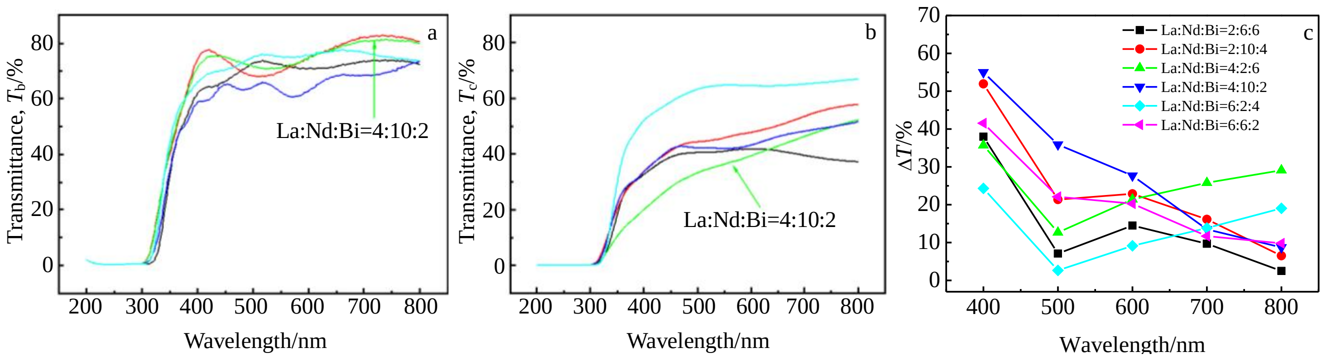

Fig.12 Transmittance curves of La, Nd and Bi co-doped TiO_2 films with different molar ratios: (a) T_b, (b) T_c, and (c) ΔT

analysis in Fig.12c shows that when the doping molar ratio is La:Nd:Bi=4:10:2, the ΔT curve of the co-doped TiO_2 film is larger, and the film coloring state/bleaching state transmittance is also larger. The optical modulation performance is also relatively excellent. It is found that the doping ratio of La, Nd and Bi is an important factor affecting the electrochromic properties of co-doped TiO_2 films.

3 Conclusions

1) Crystallinity of TiO_2 films is related to the heat treatment temperature. The lower the temperature, the higher the content of amorphous phase. When the calcination temperature is 500 ℃, the greater the co-doping amount of La, Nd, and Bi, the higher the amorphization degree of the crystal.

2) The La, Nd and Bi single-doped TiO_2 films have electrochromic properties. When the molar single-doping amount is 8% La, 18% Nd, and 6% Bi, the electrochromic performance is relatively excellent, and the order of the three single-doped electrochromic effects is 6% Bi<8% La<18% Nd.

3) TiO_2 films prepared by co-doping of La, Nd and Bi shows anatase type with high degree of amorphous phase. When the doping molar ratio is La:Nd:Bi=4:10:2, the co-doped TiO_2 film has the highest degree of amorphous phase, and its cyclic voltammetry is also the best.

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La、Nd、Bi 共掺杂制备 TiO_2 电致变色薄膜及其性能研究

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摘　要：为了提高 TiO_2 薄膜的光学属性和着色效率，采用溶胶-凝胶工艺，以钛酸丁酯为前驱体在 ITO 导电玻璃基片表面制备了 La、Nd、Bi 共掺杂 TiO_2 薄膜。采用 XRD、UV-vis 和化学工作站等手段研究了 TiO_2 薄膜的结构和表面的光学和电致变色性能。结果表明：在 400、500 和 600 ℃热处理的二氧化钛干凝胶中形成锐钛矿型二氧化钛，且热处理温度越高，晶体发育越完整。La、Nd、Bi 掺杂 TiO_2 增加了 TiO_2 八面体的排列无序性，导致非晶化程度提高。体积分数为 12%的钛酸丁酯相应制备的薄膜具有优良的电致变色性能。500 ℃热处理的 TiO_2 薄膜电致变色性能最为优异。实验进行了 La、Nd、Bi 单独掺杂 TiO_2 薄膜的性能分析，单独掺杂摩尔分数为 8% La、18% Nd、6% Bi 的 TiO_2 薄膜具有较优异的变色性能，单独掺杂变色效果的顺序是 6% Bi<8% La<18% Nd。La、Nd、Bi 共掺杂锐钛矿型 TiO_2 仍然具有很高的非晶化程度，且当掺杂摩尔比 La:Nd:Bi=4:10:2 时，取得薄膜最佳循环伏安特性，掺杂 TiO_2 非晶化程度最高。

关键词：电致变色；溶胶-凝胶法；La、Nd、Bi 共掺杂 TiO_2 薄膜；循环伏安；着色效率

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