Unraveling the Effect of Cation Types on Electrochromic Properties of Titanium Dioxide Nanocrystals

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Electrochromic (EC) devices have been regarded as promising candidates for energy-saving smart windows, next-generation displays, and wearable electronics. Monovalent ions such as H⁺- and Li⁺-based electrolytes are the benchmark insertion ions for EC devices but have serious limitations such as high cost, instability, and difficulty to handle. Seeking multivalent electrolytes is an effective alternative way to prepare high-performance EC devices; unfortunately, the related reports are currently limited to tungsten oxide EC materials. Herein, for the first time, we investigate the EC properties driven by different valence cationic (i.e., Li⁺, Zn²⁺, and Al³⁺) electrolytes in the titanium dioxide system. It is found that the initial optical modulation ranges of TiO₂ nanocrystal (NC) films in Li⁺, Zn²⁺, and Al³⁺ electrolytes are 76.8%, 77.4%, and 77.3%, respectively. After 250 cycles, the optical contrast of these films in Zn²⁺ electrolyte decreased by only 2.3%, much lower than that in benchmark Li⁺ electrolyte of 10.1% and Al³⁺ electrolyte of 59.1%. Density functional theory calculation indicates that the potential barriers of Li⁺, Zn²⁺, and Al³⁺ in TiO₂ are 0.59, 0.55, and 0.74 eV, respectively, which makes TiO₂ NCs show good EC properties in Zn²⁺ electrolytes. This work unravels the effect of different valence cations on the electrochromic properties of titanium dioxide NCs, which may provide some new directions for the development of excellent EC devices with long-term stability and durability.

1. Introduction

Electrochromism (EC) refers to the reversible variation of the optical properties (i.e., transmittance, reflectance, and absorbance) in some materials under the applied potential difference or current [1–6]. EC devices have the features of simple structure, low power consumption, flexibility, and scalability, which makes them have strong potential applications in energy-saving smart windows, next-generation displays, and wearable electronic products [7–13]. The basic working principle of electrochromism is reversible intercalation/deintercalation of foreign protons or ions in the host crystal, resulting in the redox reaction of the matrix material [14–19]. At present, there are many EC materials with Li⁺ and H⁺ as electrolytes, which have good EC properties [7, 20]. However, there are still some problems, which hinder the further development of Li⁺- and H⁺-based electrolytes: (1) Due to the toxicity, flammability, and high cost of Li⁺-based electrolytes, EC devices need a strictly controlled environment for assembly [21–23]. (2) H⁺-based electrolyte has strong corrosivity on the surface of metal oxide electrodes, which generally degrades the cycle life of EC devices [24]. In addition, due to the low electrode potential of H⁺, H₂ gas bubbles will be formed easily polarized during electrochemical reaction [18, 25]. Therefore, it is of great significance to search for alternative cheap, stable, and rapid insertion ions in EC devices to achieve cost-effective and rapid EC application.

To achieve this goal, researchers have made a lot of efforts from the perspective of a novel structure and doping modification of EC materials [2, 26, 27]. Although the EC performance of devices has been improved to some extent, the inherent problems of electrolyte optimization still exist. Recently, it has been noted that multivalent ions as insertion ion electrolytes can significantly improve the EC performance,
because the number of electrons per multivalent metal ion intercalates into the framework than Li⁺ or other monovalent ions [25, 28]. In particular, the EC device of trivalent Al³⁺ ion intercalation has attracted extensive attention because of its rich crustal storage, small ion radius, high optical contrast, safety, and reliability [21, 22]. However, due to the strong electrostatic interaction between Al³⁺ ions and the intercalation framework, there are great difficulties in the intercalation process [21, 25, 29]. So far, the reports on EC performance driven by different valence cation ions mainly focus on the classical tungsten oxide EC materials and there is a lack of systematic research on other EC materials [14, 24]. Further study on EC properties driven by different valence cations in other EC material systems will help to build high-performance EC devices.

Among the many EC materials, titanium dioxide (TiO₂) is a great potential candidate material because of its excellent physical, chemical stability, and acid resistance [30–32]. In particular, TiO₂ has been shown to have excellent EC properties in Li⁺-based electrolytes [33–35]. However, there is still no report regarding TiO₂ for trivalent ion electrochemical cells from the EC community or systematic research on EC performance driven by different valence ions yet. This is mainly due to the stronger Coulomb ion lattice interaction of multivalent ions than monovalent ions [25]. It is predicted from the thermodynamic mechanism that reducing the intercalation energy of ions can activate the reversible electrochemical behavior of materials [36]. For example, Koketsu et al. constructed a reversible multivalent ion battery with high efficiency and high capacity by introducing Ti vacancy into anatase TiO₂, which significantly reduced the intercalation energy of Mg²⁺ and Al³⁺ [37]. Recently, it is reported that tungsten doping into TiO₂ can reduce the intercalation energy of Zn²⁺ and activate its electrochromic properties [38]. Therefore, the W-doped TiO₂ provides the possibility to directly study and compare the EC behavior driven by different valence ions and is expected to bring new horizons for obtaining high-performance and stable EC devices.

In the present work, we explore the EC properties of anatase W-doped TiO₂ NCs in different valence cations (i.e., Li⁺, Zn²⁺, and Al³⁺) by in situ transmission spectroscopy and electrochemical tests. It is found that when the light modulation range of W-doped TiO₂ films in Li⁺, Zn²⁺, and Al³⁺ electrolytes is similar (76.8%, 77.4%, and 77.3%, respectively), the light modulation range of the W-doped TiO₂ NC films in Zn²⁺ electrolyte is only reduced by 2.3% after 250 cycles, which is far lower than that in Li⁺ electrolyte of 10.1% and Al³⁺ electrolyte of 59.1%. At the same time, the coloration efficiency of the film in Zn²⁺ electrolyte is only reduced by 8.7% after 250 cycles, which is much higher than that in Li⁺ electrolyte of 37% and Al³⁺ electrolyte of 90%. The results show that the Coulomb interaction between the ion radius and the ion charge significantly affects the electrochemical kinetics of W-doped TiO₂ NCs. Density functional theory (DFT) calculation shows that the potential barrier of Li⁺, Zn²⁺, and Al³⁺ in TiO₂ NCs are 0.59, 0.55, and 0.74 eV, respectively, which indicates that Zn²⁺ can bring the required fast switching, high contrast, and high stability for EC devices. The research results are of great significance to the basic research in the field of electrochromism and open up a new direction for realizing long-term stable, durable, and fast-switching devices.

2. Materials and Methods

2.1. Synthesis of W-Doped TiO₂ NCs. The synthesis process is similar to our previous paper [30]. In short, W-doped TiO₂ NCs were synthesized by heating the metal precursor salts in 1-octadecene (ODE) (90%) in a pot with an N₂ atmosphere at 280°C. 1-Octodecane (ODAL) (99%) was used as the hydroxyl supplier, and oleic acid (OA) (90%) and oleylamine (OLA) (90%) were used as the cosurfactants. Titanium ethoxide (technical grade) (1 mmol), tungsten chloride (0.2 mmol), ODE (8 mL), OLA (0.5 mL), OA (0.5 mL), ODAL (10 mmol), and ammonium fluoride (NH₄F) (0.4 mmol) were mixed in a 50 mL three-neck flask. After the mixture was degassed in a vacuum at 120°C for 20 min, nitrogen was introduced and maintained in a nitrogen atmosphere throughout the synthesis process. After the mixture was rapidly heated to 280°C, it was maintained at 280°C for 60 minutes for NC growth. After the reaction was stopped, the reaction mixture was cooled to ~60°C and the solid product was obtained by acetone precipitation and centrifugation at 7000 rpm for two minutes. The supernatant was discarded and dispersed in hexane. Finally, NCs were dispersed in toluene at a concentration of about 45 mg·mL⁻¹ for use.

2.2. Preparation of the W-Doped TiO₂ NC Film. 2 cm × 2 cm FTO glass (10Ω·sq⁻¹) was washed with 2 vol.% Hellmanex III solution for 5 minutes, then washed with deionized water for 5 minutes, and finally washed with acetone and ethanol for 15 minutes. 100 µL TiO₂ NC solution (~45 mg·mL⁻¹) was spin coated on FTO glass at 1500 rpm for 30 seconds. After drying on a hot plate at 250°C for 5 minutes, the second layer of spin coating was carried out. The spin coating process is carried out five times in total to achieve the required film thickness. To remove the organic ligands on the surface of nanocrystals, we heated the doped TiO₂ NC film deposited on FTO glass in the air at 400°C for 50 minutes (5°C·min⁻¹).

2.3. Characterization. The structure and morphology of NCs were characterized by X-ray powder diffraction (XRD) (Rigaku Corporation), transmission electron microscope (TEM) (FEI Tecnai G2 F30), and field emission scanning electron microscope (FESEM) (ZEISS Sigma 500/VP). In situ transmittance spectra of the films and devices were performed on an Avantes spectrometer (Avaspec-ULS2048CL-EVO). Electrochemical tests were carried out using an Autolab PGSTAT204 electrochemical workstation.

2.4. Electrochemical and Electrochromic Measurements. A custom three-electrode spectroelectrochemical cell was connected with an Avantes spectrometer to measure the electrochemical and electrochromic properties of doped TiO₂ NC films. The W-doped TiO₂ NC film was used as the working electrode, and platinum sheet and Ag/AgCl...
were used as counter electrode and reference electrode, respectively. 0.5 M Li$_2$SO$_4$, 1 M ZnSO$_4$, and 0.5 M Al$_2$(SO$_4$)$_3$ dissolved in deionized water are used as electrolytes to ensure that all electrolyte ions are 1 M of Li$^+$/Zn$^{2+}$/Al$^{3+}$. The transmittance of FTO glass subjected to the same heat treatment as the working electrode is used as the reference in the same electrolyte. The electrochemical impedance spectrum in the frequency range of 100 MHz to 100 kHz was measured on the electrochemical workstation (Autolab PGSTAT204).

2.5. Computation Details. The Li$^+$/Zn$^{2+}$/Al$^{3+}$ diffusion barrier in the Ti$_{14}$W$_2$O$_{32}$ structure is calculated by using the force-based optimization scheme and the climbing image propulsion elastic band (CI-NEB) method. To study the single migration of Li$^+$/Zn$^{2+}$/Al$^{3+}$ in W-doped TiO$_2$, a supercell structure of $2 \times 2 \times 1$ in pure TiO$_2$ with atomic number Ti$_{16}$O$_{32}$, two Ti are replaced with W to construct W-doped TiO$_2$, with atomic number Ti$_{14}$W$_2$O$_{32}$. Li/Zn/Al atoms diffuse from one structural position to another in the Ti$_{14}$W$_2$O$_{32}$ inner hole and increase the influence of the ion radius (Li$^+$/Zn$^{2+}$/Al$^{3+}$ = 0.60/0.74/0.53 Å) and charge. In detail, we give the diffusion barrier of Li/Zn/Al migration in titanium dioxide. It takes the initial structure (0) as the zero point, the x-axis is the distance between Li/Zn/Al atoms and the initial structure, and the y-axis is the energy of each structure minus the energy of the (0) structure. In other words, if the $y$ value is positive, the energy at this position is higher than the (0) structure, and if the $y$ value is negative, it is lower than the (0) structure.

3. Results

It is noted that there are few reports of TiO$_2$-based electrochromism driven by multivalent ions compared with Li$^+$ and H$^+$. This may be because multivalent ions have a larger size and stronger Coulomb ion lattice interaction than monovalent Li$^+$ and H$^+$ [34]. Recently, it was found that W-doped anatase TiO$_2$ NCs can significantly reduce the intercalation energy of ions and activate the reversible electrochemical behavior of known materials [38]. In this work, to explore the EC properties of TiO$_2$ driven by different valence ions, the W-doped anatase TiO$_2$ NCs were selected as the research model. The anatase TiO$_2$ NCs doped with W content (as W/[Ti + W + O]%) of 4.1 at% were synthesized by a one-pot fluorne-assisted method (see experimental details in the supplementary material). This doping content has been proved in our previous work that TiO$_2$ NCs can obtain the optimal EC light modulation range [38]. Figure 1(a) shows the typical transmission electron microscopy (TEM) images of W-doped TiO$_2$ NCs, from which it can be seen that NCs were pseudospherical. The
X-ray powder diffraction (XRD) pattern of W-doped TiO$_2$ NCs (Figure 1(b)) discourses that these NCs are typical characteristics of anatase TiO$_2$ [30, 38]. The W-doped TiO$_2$ NC solution was spin coated on FTO glass and annealed in air at 400 °C for 50 minutes to remove the surfactant and form a transparent nanoparticle thin film. Scanning electron microscopy (SEM) (Figure 1(c)) shows that W-doped TiO$_2$ NCs are densely distributed on the whole film. Figure 1(d)
shows the cross-section SEM image of the W-doped TiO$_2$ NC film, indicating that the thickness of the film is very uniform, with a thickness of 480 nm. This uniform W-doped TiO$_2$ NC film is conducive to being used as a research model to further characterize and analyze the EC properties driven by different valence ions.

To reveal the effect of different valence cations on the EC properties of W-doped TiO$_2$ NCs, a three-electrode spectroelectrochemical cell was constructed by using Li$_2$SO$_4$, ZnSO$_4$, and Al$_2$(SO$_4$)$_3$ as electrolytes, respectively (Li$^+$, Zn$^{2+}$, and Al$^{3+}$ with the same concentration of 1.0 M were used for comparison), Pt foil as counter electrode, and Ag/AgCl as reference electrode to characterize the electrochemical and EC properties of TiO$_2$ NC films. The results of X-ray photoelectron spectroscopy (Figure S1–3) and Raman spectroscopy (Figure S4) of NC films under different EC states show that the injected electrons are located in Ti$^{4+}$ during the intercalation of ions, resulting in the blue shift of the TiO$_2$ absorption band and obvious color changes. In the process of EC application, the light modulation range is a very important performance parameter. We tested the EC performance of the film in three electrolytes under the same potential windows, but the optical modulation range is quite different (Figure S5). So, similar high optical transmittance modulation (76.8%, 77.4%, and 77.3% for Li$^+$, Zn$^{2+}$, and Al$^{3+}$, respectively) was selected at 550 nm to facilitate the comparison of the effects of three valence cations on W-doped TiO$_2$ NCs [25]. Figure 2(a) shows the transmittance spectra in the fully colored and bleached state of the W-doped TiO$_2$ NC films in the three electrolytes. It should be noted here that this is the first reported EC property of TiO$_2$ driven by Al$^{3+}$. Switching time ($\tau$) is a key factor, which was defined as the time to change the full optical modulation by 90% [7]. The time-dependent transmission spectrum with a wavelength of 550 nm (Figure 2(b)) discloses that the bleaching/coloration time ($\tau_b$/\tau_c$) of the W-doped TiO$_2$ NC film in Li$^+$, Zn$^{2+}$, and Al$^{3+}$-based electrolyte are 5.7/4.8, 2.5/5.9, and 6.1/5.2 s, respectively. Specifically, the radius of Li$^+$ (0.60 Å) is small and the charge density and polarization intensity of Li$^+$ are much lower than those of Zn$^{2+}$ (0.74 Å) and Al$^{3+}$ (0.53 Å) [14, 37, 39], it is easy to diffuse in the electrode, so the coloration time of the film in Li$^+$ electrolyte is faster than that of the film in Zn$^{2+}$ and Al$^{3+}$ electrolyte. The coloration efficiency (CE) can be calculated by the formula $CE = \Delta OD/\Delta Q = \log (T_b/T_c)/\Delta Q$, where $\Delta Q$ was the injected charge [22, 40]. The CE value of the W-doped TiO$_2$ NC film (Figure S6) in Li$^+$ electrolyte (21.6 cm$^2$·C$^{-1}$) and Al$^{3+}$ electrolyte (15.1 cm$^2$·C$^{-1}$), indicating that the benchmark Li$^+$ can provide superior insertion kinetics. Figure 2(c) shows the first and 250th cyclic voltammetry (CV) curves of the film in Li$^+$, Zn$^{2+}$, and Al$^{3+}$ solutions at a scanning rate of 20 mV·s$^{-1}$. It can be seen that the film shows considerable electrochemical behavior in the first cycle of the three electrolytes but the cycle stability of the film in the Al$^{3+}$ electrolyte was significantly lower than that in Li$^+$ and Zn$^{2+}$ electrolytes. After 250 electrochemical cycles, the film in Al$^{3+}$ electrolyte showed a great capacitive loss and the loop feature in the CV curve nearly completes disappearance, indicating that the degree of insertion of Al$^{3+}$ into the W-doped TiO$_2$ framework after repeated cycles was very low, resulting in the deterioration of EC performance [25]. Therefore, after the 250 cycles, the EC modulation range of the film decreases rapidly (Figure 2(d)). It is noted that after 200 cycles of film in Al$^{3+}$ electrolyte, the transmittance of the bleached-state film increased slightly, because the NCs fell off slightly. The slight falling off of the film may be due to the volume distortion caused by the strong electrostatic force between the main skeleton and multivalent Al$^{3+}$. In contrast, the film in Zn$^{2+}$ electrolyte is similar to that in benchmark Li$^+$ electrolyte in response time and coloration efficiency and even better than that in Li$^+$ electrolyte in cycle stability (Figure 2(d)).

Table 1 summarizes the details of the EC behavior of the film in Li$^+$, Zn$^{2+}$, and Al$^{3+}$ electrolytes before and after 250 cycles. As mentioned earlier, the film in the three electrolytes showed high optical contrast in the initial cycle. After 250 cycles, the optical modulation ranges of the film in Li$^+$, Zn$^{2+}$, and Al$^{3+}$ electrolytes were reduced by 10.1%, 2.3%, and 6.1/14.8 s to 4.8/12.5, 5.9/13.8, and 5.2/4.9 s, respectively. The response time of the film in Al$^{3+}$ becomes faster after the cycling because the optical modulation range decreases sharply. For Li$^+$-driven electrophromism, the ions are degraded due to the irreversible ion capture in the TiO$_2$ host after 250 cycles, resulting in a little decrease in the light modulation range. At the same time, the “shallow” site network with a low energy barrier of TiO$_2$ allows ions to diffuse reversibly and rapidly throughout the whole film [19, 42], thus also accelerating the EC switching time. The CE of the film in Li$^+$, Zn$^{2+}$, and Al$^{3+}$ electrolytes also decreased from 23.5, 21.6, and 15.1 to 14.8, 19.7, and 15.1 cm$^2$·C$^{-1}$. The intercalation and deintercalation process of the film in Zn$^{2+}$ electrolyte is highly better reversibly than that in benchmark Li$^+$ electrolyte, indicating that the goal of rapid

|           | 1st $\tau_b$ (s) | 250th $\tau_b$ (s) | 1st $\tau_c$ (s) | 250th $\tau_c$ (s) | $\Delta T$ (%) | 250th $\Delta T$ (%) | CE (cm$^2$·C$^{-1}$) | 250th CE (cm$^2$·C$^{-1}$) |
|-----------|-----------------|--------------------|-----------------|--------------------|--------------|---------------------|--------------------|----------------------|
| Li$^+$    | 5.7             | 4.8                | 7.8             | 12.5               | 76.8         | 66.7                | 23.5               | 14.8                 |
| Zn$^{2+}$ | 2.5             | 5.9                | 10              | 13.8               | 77.4         | 75.1                | 21.6               | 19.7                 |
| Al$^{3+}$ | 6.1             | 5.2                | 14.8            | 4.9                | 77.3         | 18.2                | 15.1               | 1.51                 |
response, high contrast, and high stability can be achieved by using Zn$^{2+}$ as electrolytes in an aqueous solution.

To understand the electrochemical mechanism of W-doped TiO$_2$ NC films in different valence cationic electrolytes, the scanning rate-dependent CV was analyzed quantitatively. According to the Randles-Sevcik equation [43], the diffusion coefficients were calculated as $2.1 \times 10^{-12}$, $6 \times 10^{-13}$, and $2.1 \times 10^{-13}$ cm$^2$ · s$^{-1}$, by using the CV curve of film at the 2 to 10 mV·s$^{-1}$ scanning rate in Li$^+$, Zn$^{2+}$, and Al$^{3+}$ electrolytes, respectively (Figure S7 (a–c)) [14, 44]. The

![Figure 3: EIS curves of the W-doped TiO$_2$ NC film in (a) Li$_2$SO$_4$, (b) ZnSO$_4$, and Al$_2$(SO$_4$)$_3$ electrolytes at different temperatures. (d–f) Arrhenius diagram shows the linear relationship between the charge transfer resistance of the three electrolytes and the logarithm of the reciprocal of absolute temperature.](image-url)
results show that the insertion kinetics of Li$^+$ is the best, Zn$^{2+}$ is the second, and Al$^{3+}$ is the worst.

The electrochemical properties of the W-doped TiO$_2$ NC film in different valence cationic electrolytes were further analyzed by electrochemical impedance spectroscopy (EIS) at open-circuit voltage. As shown in Figure S8(a), the structure of the Nyquist curve of the film in the Li$^+$, Zn$^{2+}$, and Al$^{3+}$ electrolyte is the same, which is composed of an obvious semicircle in the high-frequency region and a straight line in the low-frequency region [45]. The straight line in the low-frequency range corresponds to the semi-infinite Warburg impedance, and the approximate vertical shape shows that the electrode shows good capacitive performance in the three electrolytes [46]. The semicircle diameter in the Nyquist curve shows the interfacial charge transfer resistance ($R_{ct}$) [46, 47]. The Nyquist curves were fitted by an equivalent circuit model (Figure S8(b)), indicating that the $R_{ct}$ of the film in Li$^+$, Zn$^{2+}$, and Al$^{3+}$ electrolytes are 9.9Ω, 7.9Ω, and 15Ω, respectively. The $R_{ct}$ value shows that Zn$^{2+}$ is transferred from the solution to the surface of the W-doped TiO$_2$ NC film fastest in the process of electron injection, followed by Li$^+$. While in the Al$^{3+}$-based system, the semicircular resistance of the Al$^{3+}$-based system is higher than that of the Li$^+$- and Zn$^{2+}$-based system due to the strong limitation of electrostatic interaction in redox reaction [21]. The $R_{ct}$ shows that the speed of Zn$^{2+}$ transfer from solution to the surface of the W-doped TiO$_2$ NC film during electron implantation is similar to that of Li$^+$, which is consistent with the previous results of response time and diffusion coefficient. The EIS measurements of the W-doped TiO$_2$ NC film in Li$^+$, Zn$^{2+}$, and Al$^{3+}$ electrolytes at different temperatures were also carried out (Figures 3(a)–3(c)). As can be seen in Figures 3(a) and 3(b), $R_{ct}$ in the electrolyte of Li$^+$ and Zn$^{2+}$ gradually increases with the increase of temperature, indicating that the speed of Li$^+$ and Zn$^{2+}$ transferring from the solution to the surface of the W-doped TiO$_2$ NC film decreases with the increase of temperature. In Figure 3(c), the film in Al$^{3+}$ electrolyte decreases gradually with the increase of temperature, indicating that the speed of Al$^{3+}$ transfer from solution to the surface of W-doped TiO$_2$ NC film increases with the increase of temperature. Based on this, we used the Arrhenius equation to calculate the activation energy ($E_a$) of the electrode interface of three electrolytes/W-doped TiO$_2$ NCs [48, 49]. $E_a$ can be obtained by fitting the slope ($E_a/R$) of this linear equation. To facilitate comparison, we have adopted different drawing methods, which have appeared in previous reports [48, 49]. After calculation, the activation energies of the film in Li$^+$, Zn$^{2+}$, and Al$^{3+}$ electrolytes are 2.89, 1.89, and 2.67 eV, respectively. The lower activation energy of the W-doped TiO$_2$ NC film in ZnSO$_4$ electrolyte further shows that Zn$^{2+}$ is the easiest to migrate in the NC film [48, 50]. The abovementioned data show that the low $R_{ct}$ and activation energy of the W-doped TiO$_2$ NC film in ZnSO$_4$ electrolyte promote it to show a fast electrochemical kinetic process and then show high stability of EC properties.

To further reveal the effect of Li$^+$, Zn$^{2+}$, and Al$^{3+}$ on the EC properties of W-doped TiO$_2$ electrode, the diffusion barrier of Li$^+$, Zn$^{2+}$, and Al$^{3+}$ in anatase W-doped TiO$_2$ was further calculated by the density functional theory (DFT) [36, 51, 52]. Li$^+$, Zn$^{2+}$, and Al$^{3+}$ diffusion is from one stable state to another in Ti$_{14}$W$_2$O$_{32}$ inner pores. In the calculation, we consider the effects from the ion radius (Li$^+$/Zn$^{2+}$/Al$^{3+}$ = 0.60/0.74/0.53 Å) and the charge. Figure 4 indicates the diffusion energy curve of Li$^+$, Zn$^{2+}$, and Al$^{3+}$ from a stable position to an adjacent position under the influence of their respective charges in W-doped TiO$_2$. It can be seen that the barrier energies required for the
4. Conclusions

In conclusion, we have revealed the effects of the different valence cations (i.e., Li⁺, Zn²⁺, and Al³⁺) on the EC properties of anatase W-doped TiO₂ NCs through in situ transmission spectroscopy and electrochemical tests. It is found that the initial light modulation range of the W-doped TiO₂ NC film in Li⁺, Zn²⁺, and Al³⁺ electrolytes is similar (76.8%, 77.4%, and 77.3%, respectively). The light modulation range of the film in Li⁺, Zn²⁺, and Al³⁺ electrolytes is decreased by 10.1%, 2.3%, and 59.1%, respectively, after 250 cycles of test. The analysis of the electrochemical mechanism shows that the ion radius and the Coulomb interaction between ion charges have a significant effect on the electrochemical kinetics of TiO₂ NCs. DFT calculation shows that the potential barriers of Li⁺, Zn²⁺, and Al³⁺ in TiO₂ are 0.59, 0.55, and 0.74 eV, respectively, which indicates that Zn²⁺ can bring the required fast switching, high contrast, and high stability to EC devices. The present work is of great significance to the basic research in the field of electrochromism and may open up a new direction for realizing EC devices with long-term stability, durability, and fast switching.

Data Availability

All data presented in the paper and the supporting information are available from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare no conflict of interest.

Authors’ Contributions

S.C. conceived the idea and revised the manuscript. Y.L. designed and performed the experiments, analyzed the data, and wrote the initial draft. Y.L. and L.H. contributed to the EIS tests and data analysis. X.H., R.Z., J.Z., and B.Z. were involved in the scientific discussions and provided technical support.

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Supplementary Materials

Ex-situ XPS spectra, in situ Raman spectra, real-time transmission spectra, coloration efficiency, cyclic voltammograms, and Nyquist plots of the W-doped TiO₂ NC film in Li₂SO₄, ZnSO₄, and Al₂(SO₄)₃. (Supplementary Materials)

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