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**Doped Tungsten Oxide Nanocrystals for
Next Generation Electrochromic Windows**

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**Doped Tungsten Oxide Nanocrystals for
Next Generation Electrochromic Windows**

by

Sungyeon Heo

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Dedication

To my wife shinhye for her patience and sacrifice during my entire graduate study and to my loving parents making me possible to reach here.

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Abstract

Doped Tungsten Oxide Nanocrystals for Next Generation Electrochromic Windows

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The University of Texas at Austin, 2019

Supervisor: Delia J. Milliron

Doped tungsten oxide (WO_{3-x}) nanocrystals (NCs) have lots of potential for next generation electrochromic windows compared to bulk thin films. The difference lies in intrinsic WO_{3-x} NC properties of shape and crystalline anisotropy with localized surface plasmon resonance absorption in the shorter wavelength near-infrared range, which can directly affect the major electrochromic performance of switching speed, optical modulation, and cycling stability. This work illustrates how doped WO_{3-x} NC properties are effectively utilized for enhancing the electrochromic performance. First, how shape anisotropic properties can generate highly porous film is studied using different aspect ratio of $\text{WO}_{2.72}$ nanorods. By changing the nanorod interaction to electrostatic repulsion from solution ligand-stripping chemistry, highly porous mesoporous thin film from randomly packed nanorods is fabricated. Incorporating guest inorganic materials of niobium polyoxometalate clusters followed by chemical condensation, dual-band modulation of electrochromic films on flexible substrates are demonstrated, tackling cycling stability, and optical modulation issues. Second, how doped semiconductor NCs are effectively used for dynamic Bragg stacks with targeted performance of ‘on and off’ reflectance is studied.

Dynamic reflectance tuning can affect the color tuning as well as efficient heat blocking. Judicious NC selection of indium tin oxide and WO_{3-x} NCs from mechanistic understanding of electrochemical modulation of optical properties, optimization of film processing, and reliable refractive index data from *in situ* ellipsometry enable accurate Bragg stack optimization from simulation and experimental realization. Third, using monoclinic $\text{WO}_{2.72}$ nanorods as a model system having different size of three intracrystalline tunnel sites, we study spectroelectrochemical properties with different cation system (lithium, sodium, and tetrabutylammonium ion). In doing so, Al_2O_3 atomic layer deposition is employed to prevent electrolytes degradation and allows to study spectroelectrochemical properties. Na^+ electrolytes system gives higher coloration efficiency than Li^+ electrolytes and mainly capacitive charging behavior owing to its occupancy in the hexagonal tunnel sites. The results of these studies suggest general approach to improve electrochromic performance where shape and crystalline anisotropic properties of doped metal oxide nanocrystals can be effectively utilized for impacting spectroelectrochemical properties.

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Chapter 1: Introduction

1.1 MOTIVATION OF SMART WINDOWS

About 39 % of national electricity in U.S. is consumed from buildings as shown in Figure 1.1. The most use of electricity in commercial and residential building is from lighting, heating, ventilation, and air-conditioning (HVAC).^{1,2} Among HVAC, energy consumption from lighting, heating, and air-conditioning is directly related to the sunlight. Moreover, modern buildings incorporate more and more windows because people want to see outside the world and sunlight is recognized as a best light source. However, large installation of windows makes significant impact on inefficient use of solar light related to large energy consumption.

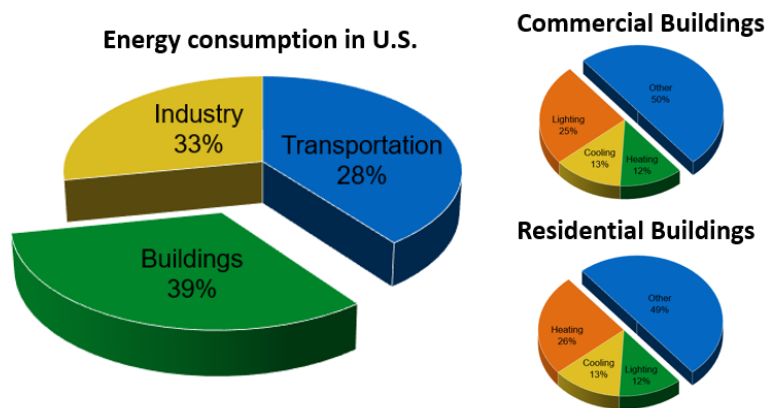


Figure 1.1 U.S. energy consumption by the sector (2011 Building Energy Data Book, U.S. DOE)

Actually, the sunlight is the best source of heating and lighting. Visible light consisting of 43% of solar energy can control the natural lighting as well as heating and near-infrared light is 52 % of the sunlight taking in charge of the heating control as shown

in Figure 1.2. The independent transmittance control of each light in the different wavelength region can make significant effect on the energy-savings in the buildings.

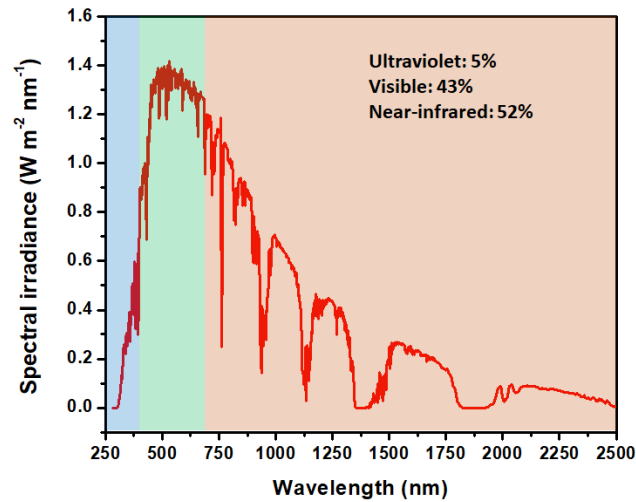


Figure 1.2 Solar energy distribution under air mass 1.5

Compared to static windows coated with low-emissive coating which cannot control the solar energy transmittance as well as have fixed gain for visible and near-infrared light no matter how weather changes, electrochromic windows which can modulate the solar transmittance can solve these issues. Deb's demonstration of electrically induced coloration process in amorphous MoO₃ and WO₃ thin films in the 1960s stimulated extensive research on a number of other transition metal oxide.³⁻⁵

1.2 OPERATION MECHANISM

There are different types of electrochromic windows such as type I (consisting of electrochromic molecules and redox reagents), type II (electrochromic molecules bound to

the metal oxide films), and type III (thin film battery-type configuration) devices.⁶ Type III device features open circuit memory of maintaining their colored state when it is open circuit potential after charging. This advantage makes this device type popular and most widely adopted in many commercial companies such as Sage Inc. and View Inc. In the rest of entire studies, type III devices will be a major focus of the research.

As name of thin film battery-type suggests, Type III electrochromic windows are composed of stack of layers consisting of electrochromic layers and ion storage layers deposited on transparent conducting oxide substrates separated from ion conducting electrolytes (Figure 1.3).

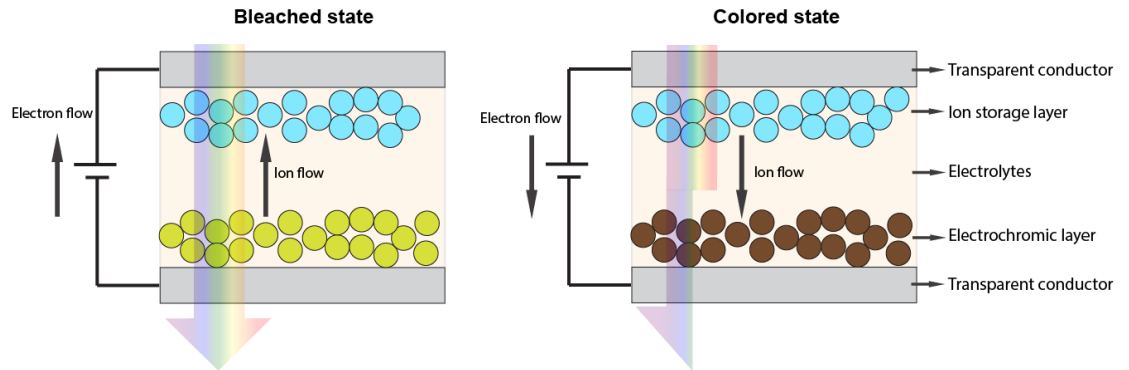


Figure 1.3 Electrochromic device configuration and its operation mechanism.

The simple operation principle is the device darkens when ions or electrons are inserted to the working electrode and device bleaches when they are extracted from the working electrode and stored into the charge storage layer.

For the electrochromic layers, cathodically coloring transition metal oxides such as TiO_2 , MoO_3 , WO_3 , and Nb_2O_5 are used. These materials have full $\text{O}2\text{p}$ band and empty d band, so the film is usually transparent. Insertion with ions and electrons provides partial

filling of d band which gives coloration properties. For the ion storage layers, optically passive materials such as CeO_2 can be used or anodically coloring metal oxide such as NiO and IrO_2 can be employed. These anodically coloring materials initially have partially filled t_{2g} states and electron insertion fully fills t_{2g} states. If the gap between t_{2g} and e_g state is wide enough, it shows the transparent states.⁷

While type III devices have in common with batteries, there are obvious differences between them making electrochromic thin films interesting and challenging at the same time. First, compared to large potential windows of greater than 3V of battery operation for high power density, electrochromic windows usually operate in the moderate potential windows of around 2.5V. This moderate potential window mitigates electrolytes degradation problem which is significant issues known as solid electrolytes interphase (SEI) in battery fields.⁸ Second, electrochromic thin films are composed of only inorganic materials, different with battery stack composed of inorganic materials mixed with binder and carbon. This simple structure makes the analysis of electrochromic films easier. Third, compared to the battery dealing with electrochemistry, electrochromic thin films cover electrochemistry with optical properties so that the film quality is important for reducing light scattering. For the same reason, the transparent conducting oxide substrates are frequently used.

1.3 MAIN FACTORS

1.3.1 Switching speed

The switching speed is mainly related to ion and electron transport in the devices. In order to achieve fast switching in the devices, condition of fast transport in the working electrode, ion storage layer, and electrolytes should be met. If the transport is too slow in one of the layers, device will show slow switching speed. The ion and electron transport issues usually come in together and structural design as well as material development should be considered at the same time.

1.3.2 Stability

Installed smart windows in the building cannot be replaced like easily replaceable battery. Assuming electrochromic windows operates one cycle per day, 20 year lifetime equates to a cycle life of 7300. Industry standard needs 50000 cycles.

In addition to electrochemical cycling stability, undesirable photochromic side effect is issue of real applications. In case of tungsten oxide which have narrow band gap around 2.6 eV, tungsten oxide can absorb the light of wavelength range less than 475 nm.⁹ So, generated holes from UV irradiation induce electrolytes degradation from hole transfer, thereby causing electrons and proton transfer to the tungsten oxide with coloration. This photochromic effect issues need to be delivered.

1.3.3 Optical modulation

More optical density change per unit injected charge and area is definitely desired. As a figure of merit, the coloration efficiency is defined as following.

$$\text{Coloration Efficiency (CE)} = \frac{\Delta \text{Optical Density}}{Q (\text{injected charge})/\text{area}} = \frac{\ln (T_{\text{bleached}}(\lambda) - T_{\text{colored}}(\lambda))}{Q/\text{area}}$$

where Q is the injected charge and $T_{bleached}$ and $T_{colored}$ is the transmittance in the bleached and colored state, respectively. This CE is typically given by the cm^2 per coulomb (C). Higher CE is desired because films having higher CE have better cycling stability and fast kinetics because less charge is required to give same optical density change.

Moreover, independent control of visible or near-infrared light can give more functionality to the windows optimized for the different weather conditions. In addition, the neutral color of dark grey color is desired for aesthetical reasons. Mixture of different materials is most widely used method to give desired color.¹⁰

1.3.4 Cost effectiveness

The growing market of smart windows necessitates more use of inorganic semiconductor materials and typical lithium electrolytes system. Therefore, less use of inorganic materials, cost-effective film fabrication, and replacing the limited resources of current lithium electrolytes system can be a viable option to reduce the cost for long term perspective. In this respect, solution processible colloidal nanocrystals are beneficial than conventional deposition process which needs high vacuum process.

1.4 CONVENTIONAL ELECTROCHROMISM

Before the development of colloidal metal oxide nanocrystals in 1990s, most of the electrochromic films are fabricated from expensive process of sputtering, chemical vapor deposition, or pressing of powder of micron-sized particles.^{11,12} Niobium oxide is one of the typical materials for blocking solar transmittance. Injected charge into the

electrochromic layers give following insertion of ions into the materials as following reactions.

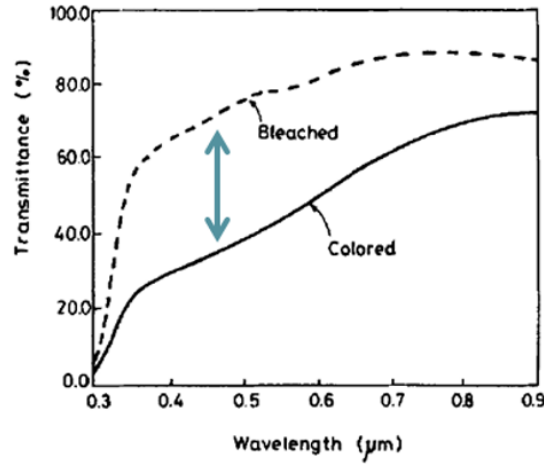
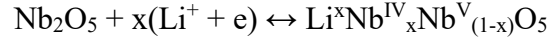


Figure 1.4 Electrochromism in amorphous Nb_2O_5

There is no unifying model of explaining the coloration of conventional materials. Most widely adopted models are polaronic absorption, introduced by Landau in 1933 and intervalence charge transfer.^{13,14} Those are basically based on electrons are localized at the certain oxidation state of ions thereby changing the oxidation state. The transfer of the electrons to other ion sites gives the coloration. Absorption wavelength range from this absorption mainly focused on the visible region with broad band (Figure 1.4). Moreover, conventional films exhibit slow kinetics because of the large diffusion length of cation intercalation into the dense thin film.

1.5. NANOSTRUCTURED ELECTROCHROMISM

The development of nanocrystal synthesis from different approaches gives opportunity to improve the performance of electrochromic windows. Owing to inherent nature of loose packing of nanocrystals, shortened ion diffusion length gives the opportunity of enhancing the switching speed. For example, diffusion coefficient of Li^+ for NbO_x films is around $10^{-13} \text{ cm}^2/\text{s}$. If the bulk film thickness is 300 nm, the diffusion time will be 4,500 sec. However, if the nanocrystal thickness is 10 nm, the diffusion time will be only 5 sec. The immense study of these nanostructured thin films for past decades made firm foundation for developing next generation of smart windows.

1.6. PLASMONIC ELECTROCHROMISM

Even though nanostructuring confers the way of increasing switching speed, using only nanostructure cannot give advanced functionality to optical modulation properties. As conventional materials give visible light modulation from polaronic absorption process, near-infrared modulation is desired for selective heating control.

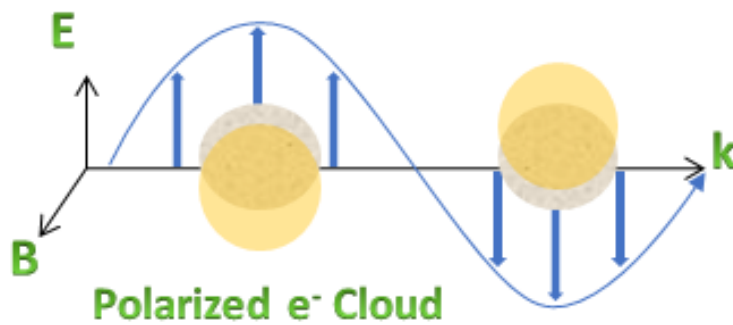


Figure 1.5 Electrochromic device configuration and its operation mechanism.

This near-infrared absorption control has been developed from plasmonic metal oxide nanocrystals.¹⁵ Compared to the metal nanoparticles having high carrier

concentration about 10^{23} cm^{-3} , doped metal oxide nanocrystals have carrier concentration around 10^{21} cm^{-3} , giving absorption peak in near-infrared region. If free electrons in the highly doped nanocrystals coherently oscillate in response to the electromagnetic field, they absorb the sunlight and it is called localized surface plasmon resonance (LSPR). This LSPR peak frequency is proportional to the bulk plasma frequency and bulk plasma frequency is tuned by the carrier density as following equation.

$$\omega_{LSPR} = \sqrt{\frac{\omega_p^2}{1+2\epsilon_m} - \gamma^2}, \quad \omega_p = \sqrt{\frac{ne^2}{\epsilon_0 m_e^*}}$$

where ω_p is the bulk plasma frequency, m_e^* is the effective mass of electrons, n is the carrier density, and ϵ_m is the dielectric constant of the surrounding, and γ is the bulk collision frequency of free carriers.

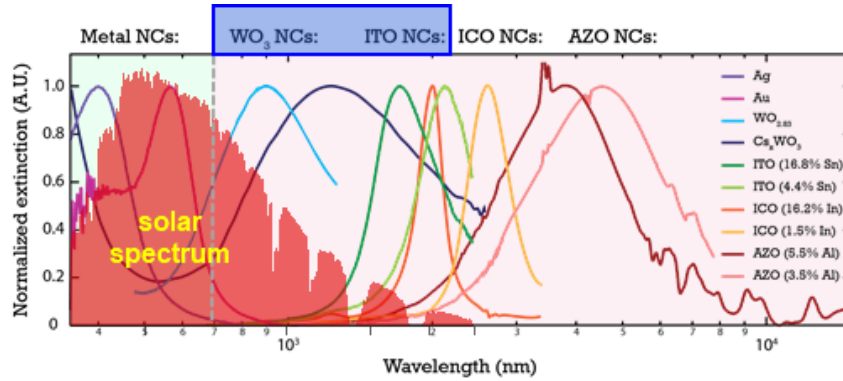


Figure 1.6 Solar spectrum and absorption of plasmonic nanocrystals.

So, LSPR optical properties can be tuned by changing the carrier density. Carrier density is typically changed by controlling the doping ratio from synthetic method. Therefore, plasmon peak is shifted depending on the different doping ratio (Figure 1.6). More important approach of tuning the LSPR properties for electrochromic applications

has been demonstrated from indium tin oxide (ITO) nanocrystal thin films by Garcia *et al.*¹³ Capacitive electrochemical charging or discharging of ITO thin films controls the carrier density by compensating the counter ions and exhibited reversible control of carrier density so that intensity and absorption peak wavelength are modulated. So, the combination of conventional materials such as NbO_x with LSPR active materials of ITO nanocrystals have been studied to show independent optical modulation in the visible and near-infrared range.¹⁶

1.7. TUNGSTEN OXIDE NANOCRYSTALS

Among different metal oxide materials, tungsten oxide is obviously prototypical material for blocking solar transmittance. When electrons are injected into the electrochromic layers, protons or ions are intercalated into the materials as following reactions.



This absorption usually contributes to the localization of electrons, so contribute to the polaronic absorption. When the nanocrystal size is reduced, most of the charging behavior happens from capacitive charging behavior. So, it gives different optical modulation behavior of LSPR absorption.

1.7.1. Crystal structure formation

Tungsten oxide is most widely studied for electrochromic materials more than 40 decades. Crystal structure is ReO₃ type perovskite structure with missing A sites. This characteristic confers interesting crystal structure formation mechanism, so-called crystal

shear mechanism.¹⁷ As oxygen vacancy increases, the crystal phase is changed by creating shear plane for incorporating the shear stress.

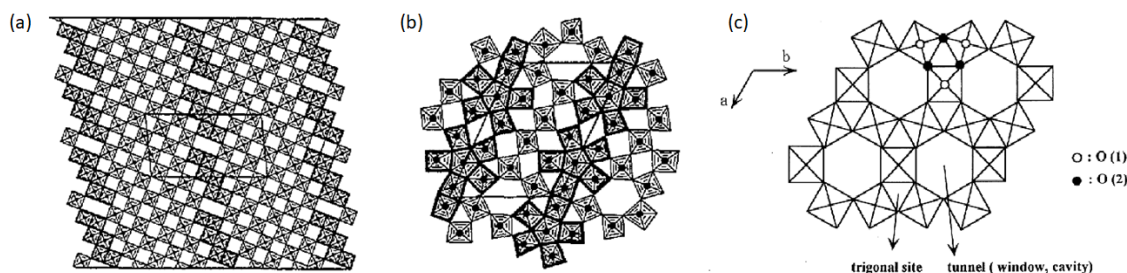


Figure 1.7 Crystal structure of (a) $m\text{-WO}_{2.90}$ (b) $m\text{-W}_{18}\text{O}_{49}$ (c) $h\text{-WO}_3$

1.7.2. Optical spectra

Even though spectroelectrochemical properties of tungsten oxide is widely studied in the bulk form, study of properties in nanocrystals is at the early stage. For the bulk form of WO_{3-x} , insulator-to-metal transition happens at $x=0.1$. Above $x>0.1$, electrical and optical properties are dominated by the free electrons.¹⁰ If tungsten oxide nanocrystals have oxygen vacancy more than 0.1, this is represented as LSPR properties. In a recent report, $\text{WO}_{2.83}$ nanorods have been shown the LSPR properties.¹⁸

1.7.3. Colloidal nanocrystals

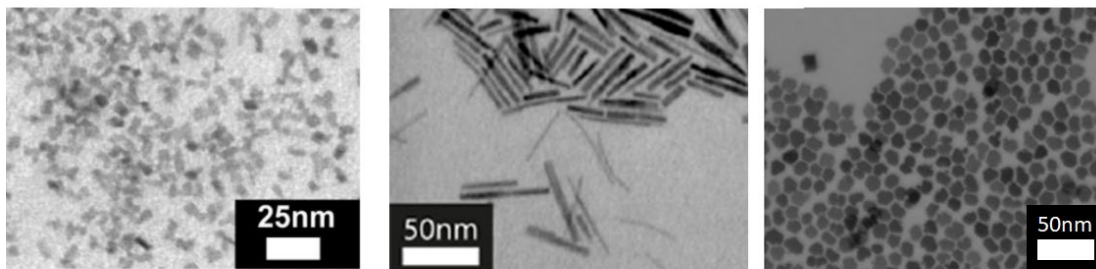


Figure 1.8 STEM images of (a) $m\text{-WO}_{2.90}$ (b) $m\text{-W}_{18}\text{O}_{49}$ (c) $h\text{-Cs:WO}_3$

Schlenk-line based air-free synthesis of colloidal nanocrystals gives precise tuning of phase, size, and doping control. From different synthetic control, cubic shaped monoclinic $\text{WO}_{2.90}$ and monoclinic $\text{WO}_{2.72}$ nanorods can be synthesized. In our recent report, different shape of anisotropic crystalline hexagonal tungsten oxide nanocrystals are synthesized to show crystal anisotropic effect on the LSPR properties.¹⁹

1.7.4. Film preparation from doped tungsten oxide nanocrystals

Electrochromic films need to be optically transparent in the bleached state which means nanocrystal stability in the solution need to be maintained during the film processing. If the nanocrystal stability is not secured during the coating process, nanocrystals are aggregated and makes cloudy films. In order to analyze the spectroelectrochemical properties exactly, film processing is very important step. Nanocrystal stability can be degraded from large size of nanocrystals or shape anisotropic property which induces strong Van der Waals attraction between the nanocrystals. Tungsten oxide nanocrystals having large amount of oxygen vacancy are easily oxidized by air exposure and precipitated. So, all the nanocrystals are processed with minimizing the air exposure.

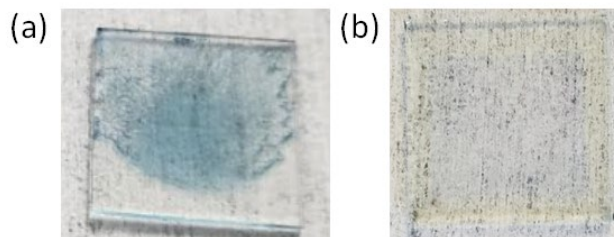


Figure 1.9 Non-uniform film with enough air-exposure (a) and uniform film with minimized air-exposure (b)

1.8 RESEARCH OVERVIEW

Tungsten oxide nanocrystals have lots of advantage for electrochromic windows. The different behavior of large portion of capacitive charging with optical modulation behavior including LSPR properties compared to traditional bulk tungsten oxide materials showing diffusion-controlled process with polaronic absorption makes nanocrystal tungsten oxide more interesting. Colloidally synthesized tungsten oxide nanocrystals have shape and crystalline anisotropic properties which can enrich spectroelectrochemical properties. However, understanding of spectroelectrochemical properties related to both anisotropic properties is at the early stage. This study can suggest general guideline for designing next generation electrochromic devices.

First part of the research is to deal with optical modulation, stability, cost effectiveness issues. The independent modulation of visible and near-infrared light has been desired for meeting different weather condition. Previous approach to deal with this problem is from nanocomposite film approach of NbO_x and WO_{3-x} .¹⁰ However, random mixing of different materials does not give fast switching speed. Approach used is to make highly porous thin films from nanocrystal assembly with block copolymer. However, this approach needs additional thermal treatment for removing organic templates. Thus, highly porous thin films without any template is desired for the application of flexible devices. In this research, we demonstrate low-temperature and template-free fabrication of mesoporous thin films of $\text{WO}_{2.72}$ nanorods that form a random, open arrangement due to their charge stabilized nature obtained by ligand-stripping. Key factors enabling fabrication of porous films are the use of anisotropic nanocrystals, specifically nanorods, and the

presence of electrostatic repulsion forces after ligand-stripping that prevent close-packing of the nanorods. High porosity up to 58% of the volume of the thin film was achieved by using long nanorods; tuning the nanorods' aspect ratios enabled control of porosity. This new process enabled low-temperature fabrication of electrochromic nanocomposite $\text{WO}_x\text{-NbO}_x$ films on flexible substrates with chemical condensation of polyniobate clusters. These films selectively modulate visible and near-infrared light transmission. This new electrochromic material simultaneously embodies the highest performing material for dual-band (visible and near-infrared) modulation and the most favorable processing conditions that can ultimately enable large scale, low cost manufacturing.

Second research is to deal with the optical modulation related to color tuning and heat blocking. Most electrochromic windows' light blocking process is based on the absorption process which allows some heat to irradiate into the room. For the color tuning process, color mixture process is most widely used process for achieving neutral color. If the dynamic tuning of the reflectance is used, it can efficiently block the heat as well as tune the color. In this research, we develop dynamic Bragg mirrors based on doped metal oxide NCs organized in periodically arranged layers of 5 nm WO_{3-x} and 15 nm 0.4 at% ITO NCs. We demonstrate 'on' (colored) and 'off' (transparent) reflection in both visible and near-infrared spectral regions. Optimized Bragg stacks were fabricated from judicious material selection and utilizing a ligand-stripping process, guided by optical simulations. To design the optimal Bragg stacks, we used measured optical constants of both WO_{3-x} and ITO NC films at different state of charge, using in situ electrochemical ellipsometric measurements, to predict the optical response of Bragg stacks using the transfer matrix

method. The fabrication of Bragg stacks constituting several layers of NC films required preparation of NC dispersions with controlled surface chemistry that controls their reliable processibility. In the end, using theoretical prediction as our guiding compass, electrochemically tunable Bragg stacks were fabricated on both ITO coated glass and flexible polyethylene terephthalate (PET) substrates, showing potential for smart window or reflector applications.

Third research is to tackle the cost issues and optical modulation. In this study, we investigate spectroelectrochemical properties of different size of cation electrolytes system of Li^+ , Na^+ , and bulky tetrabutylammonium ion (TBA^+) with focusing on the Na^+ system using m- $\text{WO}_{2.72}$ nanorods thin film as a model system. Solution phase deposition of ligand-stripped anisotropic nanorods enables fabrication of porous thin films with retention of crystal phase. Benefited from this open structure, Al_2O_3 atomic layer deposition (ALD) is employed to prevent severe electrolytes degradation on the films, confirmed from time-of-flight secondary ion mass spectrometry (TOF-SIMS) analysis as well as prevent photochromism. This passivation strategy while allowing Na^+ and Li^+ ion diffusion enables to compare different spectroelectrochemical properties. We demonstrate intermediate level of optical modulation behavior of Na^+ with strong coloration efficiency as a result of different site occupancy compared to Li^+ . For the TBA^+ , it cannot intercalate into the structure showing double-layer capacitive charging with minimum modulation.

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Chapter 2: Template-free Mesoporous Electrochromic Thin Films on Flexible Substrates from Anisotropic Tungsten Oxide Nanocrystals

This chapter has been adapted from the work “Template-Free Mesoporous Electrochromic Films on Flexible Substrates from Tungsten Oxide Nanorods, Sungyeon Heo, Jongwook Kim, Gary K. Ong, and Delia J. Milliron. *Nano Lett.*, **2017**, 17 (9), pp 5756–5761. My contribution to this work included the idea development, conducting all the experiments except GISAXS measurement, and writing manuscript.

2.1 INTRODUCTION

Nanocrystal mesoporous thin films are very promising for optical, sensor, catalyst, and electrochemical applications.¹⁻⁴ Pores increase the active surface area and simultaneously improves ion diffusion kinetics, particularly for electrochemical devices.⁵ In addition, nanocomposite systems with novel properties can be created by incorporating guest components of polymer, dye, and inorganic materials into a porous structure.⁶⁻⁸ Recent work on electrochromic nanocomposite films exemplified this approach where a $\text{WO}_x\text{-NbO}_x$ nanocomposite film fabricated by polymer templating demonstrates superior visible and near-infrared modulation coupled with unprecedented fast-switching speeds and good cycling stability.⁹

Porogens or structure-directing agents comprising of polymers or small surfactant molecules are frequently used for generating mesoporosity.¹⁰⁻¹² Careful tuning of block ratios or molecular weight of copolymer enables to control the pore dimension, porosity, and wall thickness.¹³⁻¹⁵ Porogens can also be organic ligands bound to the nanocrystal

surface needed to control growth kinetics and confer stable dispersions in the organic solvents. But annealing process to remove porogens after deposition on substrates can cause sintering of nanocrystals accompanied by irreversible changes in material properties.¹⁶ Moreover, a high temperature template removal step is not compatible with a solution-processing manufacturing paradigms that should be nominally be scalable via roll-to-roll processes onto flexible substrates.

In this respect, low-temperature template removal has been attempted to retain nanocrystal properties, lower manufacturing costs, and allow future flexible device applications. Most of approaches used so far rely on alternative treatment such as UV irradiation^{17,18}, plasma treatment¹⁹, or dissolution process by solvents with cross-linking of nanocrystals using bidendate molecules for template removal and structure retention²⁰. Ideally, these subsequent treatments of thermal or chemical processes affecting its chemical and physical properties can be avoided if mesoporous structures can be generated without any kind of templating agent, that is to say, with bare nanocrystals.

In particular, assembly of nanorods exhibited unique optical, electrical, and magnetic properties, making them good candidates for photonics and electronics applications.^{21,22} As such, a lot of research focused on ordering of nanorods, however the disordering of nanorods has been relatively underexplored in spite of the interesting opportunities of loose packing. So we hypothesized mesopores can be generated by achieving random packing of nanorods in nanoscale system.

2.2 METHODS

2.2.1 Materials

Tungsten hexacarbonyl ($\text{W}(\text{CO})_6$, 99.9%) from Strem and oleylamine (C18-content 80-90%) from Acros were used as received. Trimethylamine N-oxide (Me_3NO , 98%), triethyloxonium tetrafluoroborate (Et_3OBF_4 , 97%), *N,N*-dimethylformamide (DMF, anhydrous, 99.8%), acetonitrile (ACN, anhydrous, 99.8%), and indium tin oxide (ITO) coated polyethylene terephthalate (PET) flexible substrates with sheet resistance of $100\Omega/\text{sq}$ were purchased from Sigma-Aldrich.

2.2.2 Synthesis of different aspect ratio of tungsten oxide nanorods

Different aspect ratios of $\text{WO}_{2.72}$ nanorods were synthesized by modifying previous reported procedure.⁴⁴ For the high aspect ratios of nanorods, 1.33g of Me_3NO and 0.7g of $\text{W}(\text{CO})_6$ were dissolved in the 5.35g of oleylamine inside of glovebox. This solvent mixture in three-neck flask is heated up to 300°C and kept for 1h 30min. After the reaction was finished, solutions were transferred into the glovebox, washed with isopropyl alcohol, and redispersed in the toluene with repeated 2 times. For the low aspect ratios of nanorods, 0.9g of Me_3NO , 0.7g of $\text{W}(\text{CO})_6$, and 6.3g of oleylamine were used with same process. Both obtained low and high aspect ratios of nanorods were well dispersed in toluene at higher concentration ($\sim 80\text{ mg/mL}$) without precipitation.

2.2.3 Ligand-stripping process of tungsten oxide nanorods

Meerwein's salts (Et_3OBF_4) were dissolved in the ACN to make 60mg/ml concentration. Then Meerwein's salt solution was mixed with $\text{WO}_{2.72}$ nanorods in toluene (10mg/mL) with 1:1 volume ratio and stirred for 1 hour. After stripping, nanorods were precipitated and centrifuged at 5000rpm. The pellet was redissolved in the DMF and

reprecipitated with toluene. This process was repeated for several times to remove the excess counter ions.

2.2.4 Film processing of nanorods via spin-coating

2cm × 2cm substrates were cleaned by following process before deposition of each nanorods solutions. First, substrates were sonicated with 2 vol% hellmanex solution for 30min, cleaned with acetone and isopropyl alcohol for 30min, respectively. For the coating of as-synthesized WO_{2.72} nanorods, substrates were additionally sonicated with hexane for 30 min to make hydrophobic surface. As-synthesized ligand-capped nanorods dispersed in toluene (60 mg/ml) were spin-coated with 1400 rpm, followed by sintering at 400°C for 30 min to remove the organic ligands on the nanocrystal surface. For the ligand-stripped nanorods, one-time spin-coating of the solution with the condition of 1400 rpm for 2 min made around 300 nm-thick film by changing the solvent mixture. Layer-by-layer spin-coating method was a barrier for increasing the nanocrystal film thickness. Problem of layer-by-layer method is the condition of first layer propagates second layer, thereby compromising film quality and taking time and energy. In our experiments, DMF and ACN solvent mixture (60:40 v/v) was used considering similar dielectric constant of ACN and DMF where it affects Debye screening length. By taking advantage of low boiling point of ACN, film thickness increased to 300nm per one spin-coating (80 mg/ml) (Figure A.1 in Appendix A).

2.2.5 Preparation of WO_x-NbO_x composite films via low-temperature process

After Nb₁₀POM clusters - [N(CH₃)₄]₆Nb₁₀O₂₈·6H₂O were synthesized following previous report, guest component solutions were prepared by dissolving 80mg of

Nb₁₀POM in ethanol/DI water mixture (1:1 volume ratio).⁴⁵ 40 μ L of solutions were drop-casted onto the fabricated 300 nm-thick random mesoporous WO_{2.72} high aspect ratio nanorods film, ramped to 4000 rpm and spinned for 1min. Deposited WO_x-NbO_x composite film was dipped in 10 vol% formic acid in absolute ethanol. Chemically condensed film was rinsed with ethanol to remove the residuals. After that, thermal treatment at 150°C for 2hour was conducted in order to dehydrate the film. SEM images confirmed Nb₁₀POM were infiltrated into the entire structure while pores still exist acting as ion transport channels (Figure A.7 in Appendix A).

2.3 RESULTS AND DISCUSSION

Tungsten suboxide nanorods were selected as a model system for the following reasons. First, colloidal synthesis can tune aspect ratios by adjusting oleylamine and Me₃NO, allowing us to study aspect ratios effect on porosity. Low~7 (width: 4.3 $\pm$ 0.9, length:30.2 $\pm$ 10.1) and high~16 (width:5.3 $\pm$ 1.0, length:84.4 $\pm$ 15.1) aspect ratios of nanorods (Figure 2.1 A,B), confirmed by scanning transmission electron microscope (STEM) analysis were successfully synthesized and capped with oleylamine ligands which give steric stabilization in the organic solvents such as toluene and hexane. Nanorods were both monoclinic WO_{2.72} phase, along [010] growth direction, confirmed from X-ray diffraction (XRD) analysis (Figure 2.1C). High aspect ratios of nanorods showed intense peak from (010) plane matching with longer length of the nanorods. Secondly, WO_{2.72} nanorods not only act as basis of mesoporous films but also have functionality. Dynamic change of LSPR has been proven in the indium tin oxide nanocrystal films through electrochemical

modulation of carrier concentration.²³ Compared to other semiconductor plasmonic nanocrystals such as transparent conducting oxide exhibiting most of LSPR absorption in the short-wavelength infrared region from 1400 nm to 3000 nm, tungsten suboxide nanocrystals exhibit electrochemically tunable LSPR at the shorter wavelength region well overlapped with solar spectra.²⁴⁻²⁸ Moreover, absorbance of both low and high aspect ratios of WO_{2.72} nanorods spans near-infrared region coming from longitudinal and transverse absorption mode, making it desirable for near-infrared absorbing “smart window” materials (Figure 2.1D).

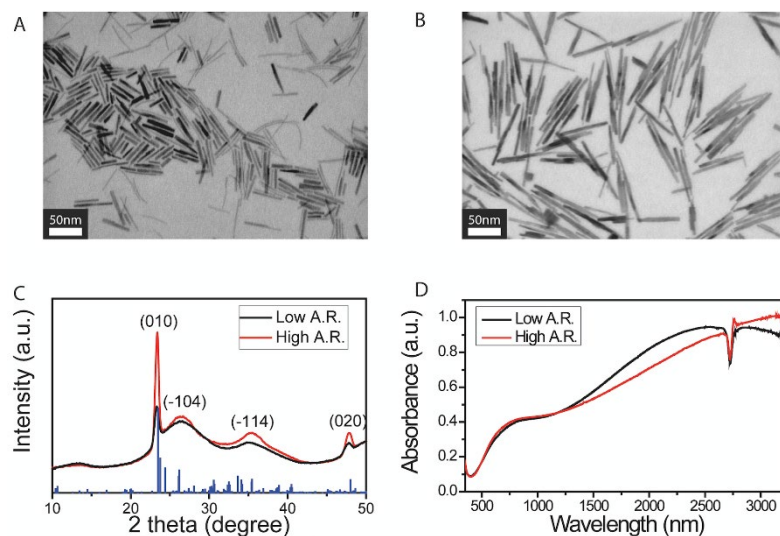


Figure 2.1 Characterization of low and high aspect ratios of WO_{2.72} nanorods. (A,B) STEM images of low (A) and high (B) aspect ratios of nanorods. (C) XRD patterns of low and high aspect ratios of nanorods and reference monoclinic WO_{2.72} pattern (ICSD code #15254). (D) UV-Visible spectra of low and high aspect ratios of nanorods dispersed in tetrachloroethylene.

As-synthesized $\text{WO}_{2.72}$ nanorods capped with oleylamine dispersed in toluene were deposited by spin-coating to check nanorods arrangement with bound ligands. Compact structure of side-by-side packing was observed as previous reports of spin-coated ZnO and boehmite nanorods (Figure 2.2A,B).^{22,29-30} This can be explained by the increase in the solution concentration from solvent evaporation inducing side-by-side packing from dominant van der Waals attraction.³¹ Both in-plane alignments and tilted domain were also observed from cross-section scanning electron microscope (SEM) measurement (Figure A.1 in Appendix A). These tilted-aligned domains were formed during the deposition process, not from original solution based on small-angle x-ray scattering analysis of original solution showing no noticeable peak from structure factor (Figure A.2 and A.3 in Appendix A). Possible explanation of tilted-aligned domain can be critical concentration of nucleation for nanorods aggregation reached before solution thins down to nanorods length, followed by radially tilted from centrifugal force.²⁹

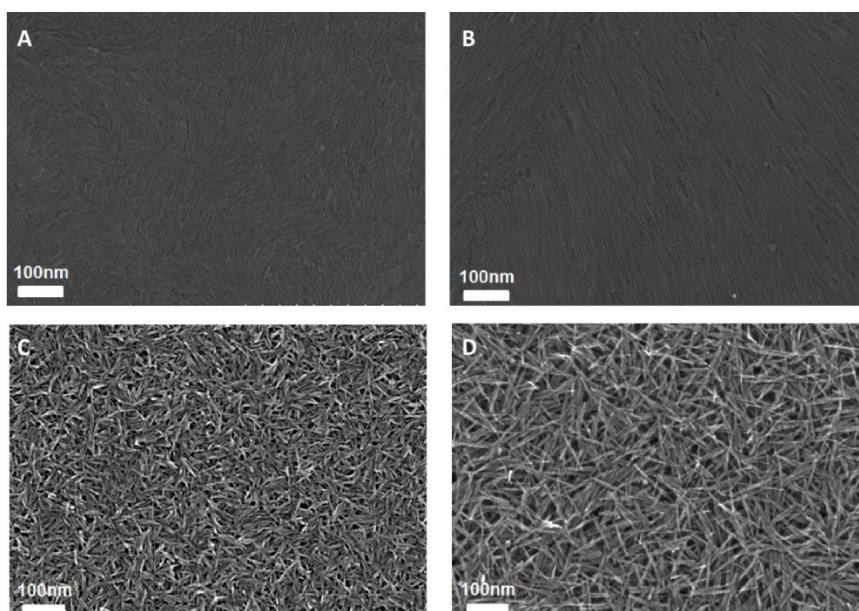


Figure 2.2 SEM images of ligand-capped and ligand-stripped low and high aspect ratios of nanorods films. (A,B) Low and high aspect ratios of ligand-capped nanorods films. (C,D) Low and high aspect ratios of ligand-stripped nanorods films.

Above packed films were capped with insulating ligands which limit the charge transport. Even though these long ligands can be exchanged with short ligands in assembled films to increase transport properties, method done after film deposition restricts the possibility of changing the interaction between nanorods.²³ Actually, ligands can also be removed in the solution before film processing so that we can exploit the changed interaction from steric stabilization to electrostatic repulsion as well as bare nanocrystals optimized for template-free method.³¹ We anticipated ligand-stripping from the nanocrystal surface changes the repulsive force so it might affect final nanorods distribution on substrates.

NOBF₄ has been introduced as a general reagent for removing native ligands from metal oxide nanocrystals.³² However, strong Lewis acidity of the nitrosonium cation influences etching of certain nanocrystals such as tungsten oxide and ZnO. So Meerwein's salt (Et₃OBf₄) was introduced having nonacidity for preventing from etching of WO_{2.72} nanorods surfaces.³³ Ligands removal was checked from fourier transform infrared (FTIR) spectroscopy after ligand-stripping. After treatment with the Meerwein's salt, complete removal of ligands was confirmed from the absence of CH₃ stretching mode around 2900nm⁻¹ from oleylamine (Figure 2.3A). One of the interesting feature, also observed in the ligand-stripped PbSe nanocrystals, is there is no stretching band of BF₄⁻ around 1080 cm⁻¹ and carbonyl stretching mode from solvent molecules of DMF around 1650 cm⁻¹. These are known for coordinating bare nanocrystal surface having positive zeta potential from dangling bond.³¹ This can be explained from zeta potential measurement in our case. After stripping ligands, surface zeta potential shifted to a negative value of around -50 mV (Figure 2.3B). Assuming that surface charge is negative, weakened coordination by BF₄⁻ and DMF is not surprising. Ligand-stripped WO_{2.72} nanorods were stable more than a month due to strong electrostatic repulsions. This negative potential is contrary to previous positively charged ligand-stripped nanocrystals.³² XPS analysis before and after ligand-stripping informed us that O/W ratio increased after ligand-stripping, so we surmised nanocrystal surface after stripping was hydroxylated (Figure A.4 in Appendix A). This negative zeta potential result makes sense assuming isoelectric point of tungsten suboxide nanorods is low around pH1.³⁴

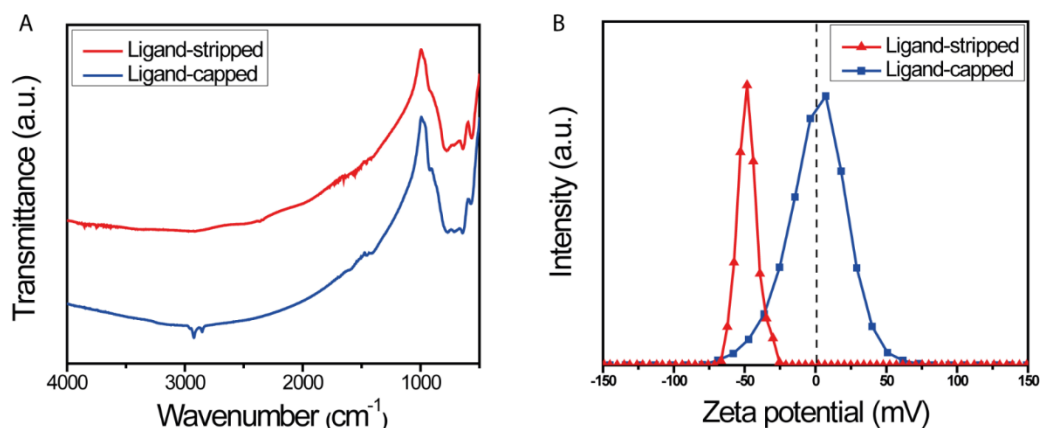


Figure 2.3 Surface characterization of ligand-capped and ligand-stripped tungsten oxide nanorods. (A) FTIR spectra for WO_{2.72} nanorods films on CaF₂ window before and after ligand-stripping. (B) Zeta-potential of WO_{2.72} nanorods before and after ligand-stripping.

Compared to the case of ligand-capped nanorods, mesoporous structure associated with random orientation of nanorods was fabricated from deposition of ligand-stripped charged-stabilized nanorods (Figure 2.2 C,D and Figure A.1 and A2 in Appendix A). The obtained films were optically clear without scattering aspect and macroscopically uniform, implying the uniform distribution of nanorods and the subwavelength size of pores. Considering its promising application to optical materials and devices, such an optically clear film, which could not be readily reached with micron or sub-size particles due to its poor dispersion and large size, is highly desirable.^{35,36} Long range random arrangement of ligand-stripped nanorods was also confirmed by grazing-incidence small-angle X-ray scattering analysis (Figure A.3 in Appendix A). Ligand-stripped films didn't exhibit

structure factor which means no particular orientation of nanorods. However, there is structure factor indicating some arrangement of nanorods for packed films.

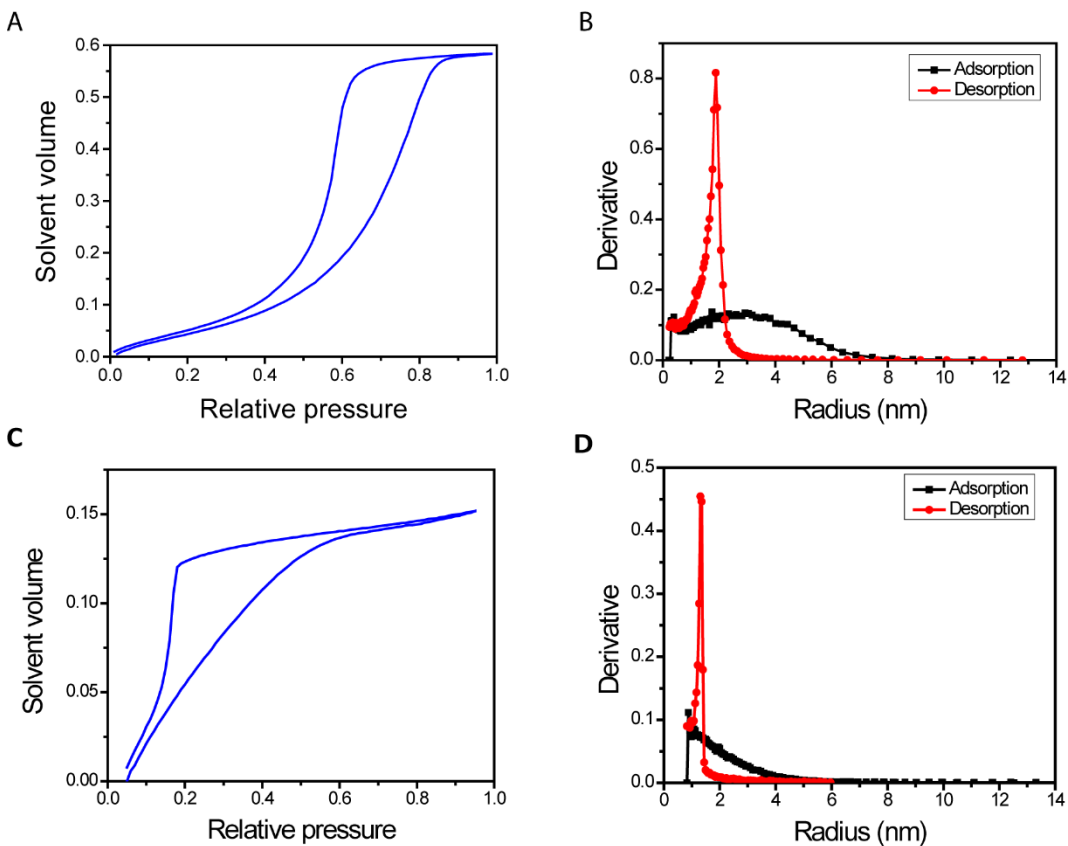


Figure 2.4 Porosity and pore size distribution of random mesoporous films from ligand-stripped nanorods measured by EP. (A,C) Porosity of high (A) and low (C) aspect ratios of nanorods random film. (B,D) Pore size distribution of high (B) and low (D) aspect ratios of nanorods random film.

The random orientation of the charge-stabilized nanorods and their mesoporous packing is possibly originated from electrostatic repulsions after stripping, which prevents the side-by-side packing even with solution concentration increase during the spin-coating

process. Considering the randomly packed arrangement of our nanorods in the final state, we assumed the nanorods were kinetically trapped, that is to say, not overcoming the energy barrier to the primary minimum of packed structure.³⁷ Slow solvent evaporation experiments of drop-casting and spin-coating further confirmed our hypothesis giving more denser packing structure (Figure A.5 in Appendix A).

Ellipsometric porosimetry (EP) measurement was employed for checking nanorods aspect ratios and arrangement effect on the porosity and pore size distribution.³⁸ This method uses the refractive index change of thin films with gradual adsorption and desorption of the solvent, thereby circumventing destruction of the nanostructure on the substrates. For the packed structure, both low and high aspect ratios of nanorods films exhibited limited porosity of 16% and porosity was not much different with high and low aspect ratios of nanorods films (Figure A.6 in Appendix A). By contrast, aspect ratios dramatically influenced on the porosity of randomly oriented films. Random arrangement of nanorods made changes where high aspect ratios of nanorods exhibited higher porosity (58%) than low aspect ratio of nanorods (15%), confirming the aspect ratio effect on the porosity (Figure 2.4 A,C). The impact of different aspect ratios of nanorods well corresponds to the experiments using macroscopic scale raw spaghetti in the beakers.³⁹ As length of spaghetti increases, packing density decreases, namely, porosity increases. Philipse also conducted similar experiments confirming the simple mathematical random contact equation, which agrees with previous experimental results.⁴⁰ This tells us to control the porosity by using different aspect ratios of nanocrystals. The porosity obtained with randomly oriented high aspect ratios nanorods is even higher than that of the mesoporous

structure by the templated approach using isotropic nanocrystals.¹⁵ Observed hysteresis of toluene adsorption and desorption branch closely related to the pore structure is type H2. This shows steep desorption branch, also observed in the porous Vycor glass characterized as irregular pores in which case interconnected networks effects are important.^{41,42} Although absolute pore radius may not be precise owing to the necessity of assuming cylindrical geometry for fitting the data, given the structural similarity of two samples, at least qualitative comparison can be made. In this framework, the data shows the pore radius increased with the porosity when the nanorod aspect ratios increased (Figure 2.4 B,D).

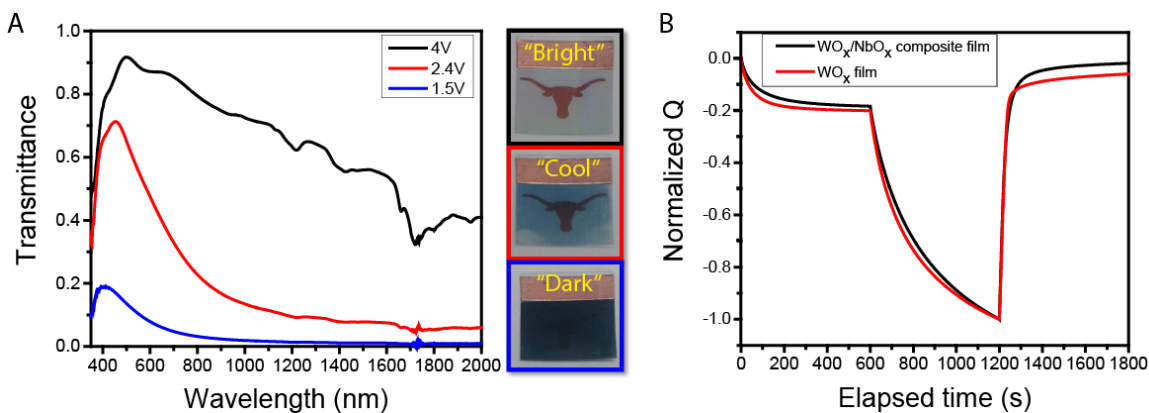


Figure 2.5 Spectroelectrochemical performance of low-temperature processed inorganic composite films. (A) In-situ transmittance spectra and its corresponding photographs of WO_x-NbO_x composite thin films on the ITO/PET substrates at each potential [4V(bright), 2.4V (cool), 1.5V (dark)] (B) Normalized charging and discharging profiles following potentiostatic steps (2.4V, 1.5V, 4V) [vs Li/Li⁺ in 1M Li-TFSI/tetraglyme]

Furthermore, these mesoporous films can be a platform for designing various nanocomposite films. One example is composite electrochromic devices. Taking advantage of low-temperature template-free mesoporous film fabrication illustrated before,

300 nm-thick films using high aspect ratios of $\text{WO}_{2.72}$ nanorods were successfully fabricated onto the tin-doped indium oxide (ITO) coated polyethylene terephthalate (PET) substrates. Combining this approach with recently published low-temperature process to chemically condense niobium polyoxometalate clusters $[\text{Nb}_{10}\text{O}_{28}]_6^-$ (Nb_{10}POM), inorganic electrochromic composite films were fabricated, absent of high temperature annealing procedures on flexible substrates.⁴³ In-situ spectroelectrochemical studies of this composite film showed selective modulation of visible and near-infrared region depending on the different charging potential (1.5V, 2.4V, 4V) (Figure 2.5A). Under 4V (“Bright mode”) [vs Li/Li^+], transmission of the film is high at both visible and near-infrared region as WO_x and NbO_x are discharged. When 2.4V (“Cool mode”) is applied, transmittance in the near-infrared region is decreased because of charging of WO_x matrix, blocking the solar heat gain while maintaining the visible transmittance which is good for daylighting. At 1.5V (“Dark mode”), NbO_x are intercalated with Li ions so the visible transmittance also decreases by polaronic absorption process. At this stage, WO_x is also further charged so that the film also blocks the light and heat. The color indices (CIELab space: $L^*=42.6$, $a^*=-1.1$, $b^*=-22.5$) at dark mode indicate blue-gray color, aesthetically desirable. When it is under discharging at 4V, the composite film shows fast discharging kinetics as same discharging speed with the WO_x only film (Figure 2.5B). This confirms existence of interface between WO_x / electrolyte/ NbO_x facilitating the ion extraction, differentiating the random mixture of WO_x and NbO_x . Compared to the WO_x and NbO_x only films, losing 60% and 30% charge capacity, respectively, the composite film also shows excellent cycling stability over 2000 times, (Figure A.8 in Appendix A).

2.4 CONCLUSION

New methodology is exemplified to achieve fabrication of uniform, mesoporous thin films by exploiting the anisotropic $\text{WO}_{2.72}$ nanorods. Changing the initially ligand-capped colloidal dispersion of nanorods to a charge-stabilized dispersion of naked nanorods by ligand-stripping allowed depositing nanorods with random orientation thereby creating large volumes of pores. This low-temperature and template-free process enables to retain nanocrystal properties as well as give possible opportunity to be applied to flexible substrates. Moreover, pore size and porosity can be controlled from using nanorods with different aspect ratios controllably synthesized. This mesoporous thin films from anisotropic nanocrystals can be a future solution to the flexible system. As an example of a mesostructured composite system made by this method, a flexible $\text{WO}_x\text{-NbO}_x$ composite films were fabricated and its fast dual-band switching kinetics was demonstrated. Other anisotropic nanocrystals such as nanoplatelet will be an option though nanorods are tested as an example of anisotropic system. This methodology can not only broaden the existing method but also enable highly mesoporous thin film in wearable, flexible, and disposable devices.

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Chapter 3: On/Off Tunable Electrochromic Bragg Stacks from Doped Semiconductor Nanocrystals

3.1 INTRODUCTION

Dynamic tuning of reflectance and transmittance in the visible and near-infrared spectral regions is important due to its potential applications to sensors,¹⁻⁴ camouflage platforms,^{5,6} advanced reflective displays,^{7,8} and military purposes,⁹ besides energy-efficient smart windows for buildings and transportation.^{10,11} Nature provides inspiration to design dynamic optical system that uses structure alongside chemistry to induce optical response. Examples can be found in organisms like squids,¹² chameleons,¹³ and beetles¹⁴ evolved to rapidly camouflage themselves in response to external stimuli. The Bragg stacks, a prototypical photonic structure, are a periodic arrangement of layers of different optical constants, creating so-called photonic stop bands inhibiting the propagation of certain wavelengths of light. The dynamic tuning photonic crystals, even simple one-dimensional structures, has inspired researchers for decades.¹⁵⁻¹⁷

Two essential optical characteristics of Bragg stacks (maximum reflectance and center peak energies of the photonic stop bands) depends upon the refractive index (RI) contrast between the material constituents, the geometric thickness of each layer, and the number of the unit cells in the stack.¹⁸ So dynamic tuning of Bragg stacks with a given number of unit cells can be performed by changing the RI contrast or the thickness of each layer in the unit cell. The most widely adopted strategies for dynamically tuning Bragg stacks is from modulating RI contrast, in the case of inorganic materials, or thickness, in

the case of organic materials. In either case, the modulation is often triggered by changing the medium occupying the void space in each layer with different vapors or solvents.¹⁹⁻²² This method has been mainly suggested for application in sensors. However, the strategy for modulating Bragg stacks based on replacing the medium is not readily adapted for integration in other contexts that require a closed system.

Another approach to tuning the RI contrast that can operate in a closed system is addition and extraction of electrons or ions to the materials in a Bragg stack by electrochemical stimuli. The materials' dielectric constants without replacing the medium can be rapidly and reversibly changed by electrochemical charging.²³⁻²⁴ An innovative strategy for tuning the transmitted color and potential for energy savings of smart windows is from implementation of electrotunable Bragg reflectors. Tunable Bragg reflectance in Bragg stack-based smart windows has the potential to realize better energy efficiency compared to current technologies that rely on absorption process alone, which allows some heat to irradiate into the inner space. Redel *et al.* demonstrated tunable electrochromic Bragg stacks in the visible region using WO₃ (cathodic coloration) and NiO (anodic coloration) nanocrystals (NCs) as the constituent materials.²³ However, since NiO and WO₃ show visible absorption under complementary conditions, all states of these Bragg stacks have shown substantial tinting, hampering potential window applications. For smart windows or other dynamic optical applications, reflection and transmission modulation with targeted performance are required and the ability to a highly transparent “off” state with low reflection and absorption is highly desirable.

It is essential to understand the RI contrast between the component materials in variable state of charge in order to design a dynamic electrochromic Bragg stack with favorable optical modulation. However, realization of Bragg stacks and the deliberate design of desirable optical properties at different electrochemical state of charge has been hindered due to following factors: 1) limited knowledge of changes in dielectric properties under electrochemical modulation, 2) poor control over NC film deposition methodology enabling deposition of periodic layers of different metal oxide NC films, and 3) poor ionic and electronic conductivity of thick Bragg stacks that contain several layers so that resistance of the stack inhibits effective optical switching.

The facile processability, synthetic tunability, and dynamic optical properties of plasmonic metal oxide NCs are well-suited for overcoming these challenges. It has been shown the infrared absorption of these materials due to localized surface plasmon resonance (LSPR) originating from free carrier density can be dynamic modulated by an applied electrochemical bias, so this class of materials has emerged as promising for fast-switching, spectrally tunable electrochromic windows.²⁵⁻²⁷ LSPR absorption directly affects the RI and understanding of electrochemical modulation of LSPR in doped metal oxide NCs has recently been more firmly established.^{28,29} Therefore, doped semiconductor NCs offer opportunities for deliberately designing tunable electrochromic Bragg stacks. There are very few reports so far where LSPR active NCs have been used as the material constituent of photonic crystals.^{30,31}

3.2 METHODS

3.2.1 Materials

Tungsten (IV) chloride (WCl_4 , 97%) was purchased from the Strem chemicals. Tin (II) acetate, indium (III) acetate, triethyloxonium tetrafluoroborate (Et_3OBF_4 , 97%), nitrosyl tetrafluoroborate (NOBF_4 , 95%), oleic acid (technical grade, 90%), oleyl alcohol (technical grade, 85%), *N,N*-dimethylformamide (DMF, anhydrous, 99.8%), oleylamine (technical grade, 70%), toluene (anhydrous, 99.8%), acetonitrile (ACN, anhydrous, 99.8%), 2-propanol (IPA, anhydrous, 99.5%), reagent alcohol (88-91%), hexane (98.5%), and indium tin oxide (ITO) coated polyethylene terephthalate (PET) flexible substrates with sheet resistance of $100\Omega/\text{sq}$ were purchased from Sigma-Aldrich. ITO coated glass substrate with sheet resistance of $200\Omega/\text{sq}$ were purchased from Diamond Coatings.

3.2.2 Synthesis of WO_{3-x} and ITO NCs

Each NCs were synthesized by modifying previously reported processes with standard air-free Schlenk line technique. First, average size of 5 nm WO_{3-x} NCs were synthesized by hot injection of 720 mg of WCl_4 dissolved in 7.096 g of oleic acid, prepared in the glovebox, into degassed 35.48 g of oleic acid and 3.24 g of oleylamine mixture at 300°C and reacted for 20 min.²⁹ The washing process was done with IPA/toluene as antisolvent/solvent in the glovebox. For the ITO NCs, 15 nm sized 0.4 at% Sn-doped ITO NCs were chosen to minimize the change in optical constants in the visible and near infrared range under applied potential.^{28,33} Indium oleate solution was prepared with degassing 1.1894 g of indium acetate and 5.78 mg of tin acetate in 9 mL of oleic acid at

140°C for 2 hours. Then, 7 ml of metal oleate solution was slowly injected at the rate of 0.2 mL/min into 12 mL of oleyl alcohol at 290°C. After cooling, the solution was washed with reagent alcohol/hexane as antisolvent/solvent.

3.2.3 Ligand-stripping of WO_{3-x} and ITO NCs

Ligand-stripping was done by following previously reported procedures.^{36,45} For the ITO NCs, NOBF₄ in DMF (10 mg/ml) was mixed with the NCs dispersed in hexane (10 mg/ml). After overnight stirring, NCs were washed several times with toluene/DMF as antisolvent/solvent. For the WO_{3-x} NCs, Meerwein's salt (Et₃OBF₄) in ACN (30 mg/ml) was mixed with NCs dispersed in the toluene (10 mg/ml). After stripping, the NCs were washed with toluene and DMF in the glovebox.

3.2.4 Deposition of NC films for in situ ellipsometry measurement

Uniform WO_{3-x} and ITO NC thin films with 100-200 nm thickness for in situ electrochemical ellipsometry were fabricated on the gold-coated highly doped silicon substrates and treated at 150°C or 300°C in an oven, applying the same conditions as the corresponding Bragg stack samples. Cyclic voltammetry of NC films on highly doped silicon substrates doesn't exhibit similar electrochemical behavior as films on ITO substrates, which might be expected from the lower conductivity of the silicon substrates (Figure B.6 in Appendix B), while gold-coated silicon substrates show similar electrochemical behavior compared to ITO substrates.

3.2.5 Ellipsometric porosimetry (EP) analysis

In order to calculate porosity of NC thin films, a J.A. Woollam M-2000 spectroscopic ellipsometer DI with an 'environmental cell' attachment was employed.

Analysis was carried out following our group's previous reports.³⁷ Toluene solvent pressure was varied inside the sample chamber while monitoring the change in optical properties in-real time. Using two Lorentz oscillators and one Gaussian function along with a Gen-Osc function, analysis of optical constants was done with CompleteEASE software ranging from 350 nm to 1690 nm. Calculation of porosity was done based on the Lorentz-Lorentz equation.

3.2.6 *In situ* electrochemical ellipsometry measurement

In order to get optical constants of each NC thin film at different potentials, *in situ* electrochemical ellipsometry measurement using the J.A. Woollam M-2000 spectroscopic ellipsometer DI with a '2 mL electrochemical liquid cell' attachment was performed (Figure B.1 in Appendix B). As prepared, each 100-200 nm thick WO_{3-x} or ITO NC film was mounted in the liquid cell chamber with Li foil as counter and reference electrodes and 1 M LiTFSI in tetraglyme as the electrolyte without air exposure. A S200 Biologic potentiostat was used for electrochemical measurements. Before optical measurement, each film was cycled chronoamperometrically between 1.5 and 4 V for 5 cycles. Charging potential was varied from 4 to 1.5 V in 500 mV steps and ψ and Δ data were measured *in situ* after 5 min charging time at each potential to assess the electrochemical equilibrium state.

3.2.7 Analysis of optical data from *in situ* electrochemical ellipsometry

The ellipsometric data analysis was done based on the different model stacks, which varied depending on the final annealing process. The thickness of the underlying gold films and the optical constants of electrolyte solutions were obtained from ellipsometry, NC film

thickness was obtained by profilometry, and porosity was determined by EP. Those values were used as inputs to determine the fitting variables. For the 150°C annealed samples, 1. silicon, 2. gold, and 3. NCs with electrolyte were considered as the layers in the stack. For the 300°C annealed samples, 1. silicon, 2. gold, 3. a thin layer of NCs embedded in the gold layer, and 4. NCs with electrolyte were considered as the layers in the stack (Figure B.2 in Appendix B). For the layer of NCs with electrolyte, an effective medium approximation (EMA) was employed considering the infilling volume of electrolyte which was set equal to the pore volume obtained from EP. For the NCs, different models for each material was employed. The Drude model for LSPR and a Tauc-Lorentz model for the interband transition were used within a Maxwell-Garnett effective medium approximation (EMA) for both 150°C and 300°C annealed ITO NC thin films for all the charging potential from 4 to 1.5 V. The fitting procedure for both 150°C and 300°C annealed WO_{3-x} NC thin films at applied potential from 2.5 to 1.5 V was conducted using a Drude model, two Lorentzians (consistent with the potential for polaronic absorption), and a Tauc-Lorentz model for the interband transition within a Maxwell-Garnett EMA, while both 150°C and 300°C annealed WO_{3-x} NC thin films at applied potentials from 4 to 3 V were analyzed with one Lorentzian and a Tauc-Lorentz model.

3.2.8 Transfer matrix method

Simulation of transmittance and reflectance data was processed with the transfer matrix method widely adopted for multilayers optical architectures. In brief, this method takes into account the light propagation through each layer considering its phase change and the boundary conditions on the amplitude at the boundaries between each pair of

adjoining layers consistent with the Maxwell equations.⁴⁷ For the optical modeling, thickness of each layer, optical constants of each layer, and the number of bilayers were used as inputs. The matrix relating the continuity of amplitude at each interlayer boundary is described by

$$A_{ij} = \frac{1}{2u_{ji}\beta_j} \begin{bmatrix} \beta_i + \beta_j & \beta_j - \beta_i \\ \beta_j - \beta_i & \beta_i + \beta_j \end{bmatrix}$$

where i, j are each layer at the boundary, θ_i , θ_j are the angles in the each layer satisfying Snell's law, n_i is RI of layer i, TE: $\beta_i = n_i \cos \theta_i$, $u_{ji} = 1$,

TM: $\beta_i = n_i \sec \theta_i$, $u_{ji} = \left(\frac{\cos \theta_j}{\cos \theta_i} \right)$.

And the matrix describing the phase difference is

$$P_m = \begin{bmatrix} e^{-i\varphi_m} & 0 \\ 0 & e^{i\varphi_m} \end{bmatrix}$$

where m indicates each layer, c is the speed of light, w is angular frequency, θ_m is the angle of incidence, φ_m is the phase difference, d_m is thickness of layer, $\varphi_m = k_m d_m$, $k_m = n_m \left(\frac{w}{c} \right) \cos \theta_m$.

From amplitude and phase change consideration, the incidence radiation with final outgoing light with full transfer matrix can be connected.⁴⁰ As we use unpolarized white light, the TM and TE were averaged for the simulation.

3.2.9 Fabrication of Bragg stacks

All the film processing was done by spin-coating ligand-stripped NCs dispersed in AN/DMF 1:1 (v/v) mixture. Before processing Bragg stacks, the target thickness was carefully met in single layers by adjusting the concentration. For Bragg stacks treated with

a final annealing step at 300°C, each layer was spin-coated at 1200 rpm for 2 min, followed by 4000 rpm for 1 min. After each deposition, the substrate was placed on the hot plate at 250°C for 5 min. These processes were repeated until the target layers were obtained, followed by a final annealing process in an oven at 300°C for 30 min. For Bragg stacks with the low-temperature annealing process, samples were fabricated either on ITO-coated glass for in situ measurement or on ITO-coated PET flexible substrates. Each layer was spin-coated with the same conditions as the 300°C annealed samples. All multilayer spin-coating were processed without removing the substrates from the chuck of the spin-coater. After that, the sample annealing was done at 150°C for 1 hour to oxidize.

3.2.10 *In situ* spectroelectrochemical measurement

Transmittance and reflectance were measured with a home-built in situ spectroelectrochemical apparatus. Fabricated Bragg stack films on ITO-coated glass substrates were immersed in an electrolyte solution composed of 1 M LiTFSI in tetraglyme. The samples were fixed while a white light was sourced at different AOIs. Reflectance and transmittance were measured by changing the detector position. A glass substrate and protected silver mirror (Thorlabs, PFR10-P01) were used for the background in transmittance and reflectance measurements, respectively. For the transmittance measurements, near 0, 30, and 45 degree AOIs were tested, and for the reflectance measurement, near 30 and 45 degree AOIs were tested.

3.3 RESULTS AND DISCUSSION

3.3.1 Materials selection: ITO and WO_{3-x} NCs

Regarding the materials selection, a promising class of materials can be colloidally synthesized doped semiconductor NCs for the design and fabrication of tunable photonic crystals. First, colloidal synthesis is well known to facilitate control over optoelectronic properties by manipulation of NC morphology and doping concentration.^{32,33} Second, dynamic modulation of infrared LSPR absorption of doped semiconductor NCs from applying a variable electrochemical potential is well established, with recent reports establishing its dependency on the NC doping concentration, size, and morphology.^{28,29}

A very important factor determining optical properties of Bragg stack is the RI contrast between the constituent layers. If the RI of all the constituent materials is well matched, the mesostructured film will not show a photonic effect, while large RI contrast induces substantial reflection. Based on this fundamental design principle, we sought to design tunable Bragg stacks that have a highly transparent off state and reflect light in the on state; WO_{3-x} and ITO NCs were selected as they are well-suited for this objective. For the purpose of maximizing the reflectance in the charged (on) state, oxygen vacancy-doped cubic-shaped WO_{3-x} NCs were selected because their absorption lies in the relatively shorter wavelength NIR region that strongly affects solar control and, based on the absorption tail, color. 5 nm sized cubic-shape NCs have also been shown to strongly modulate transmittance when electrochemically charged confirmed from high coloration efficiency ($103 \text{ cm}^2/\text{C}$ at 1000 nm), as may be expected from small size.²⁹ Having selected WO_{3-x} NCs as base material for one layer in the periodic lattice of the Bragg stack, ITO NCs were chosen as the complementary material based of the following criteria. First, minimizing the RI contrast between the constituent materials in the off state is necessary.

ITO has a similar bulk RI (2.19) to that of tungsten oxide (2.1). Second, since WO_{3-x} exhibits a large modulation of RI with state of charge in visible range (vide infra), minimizing the modulation in RI of the complementary material is necessary so as to maximize RI contrast in the charged state. Zandi *et al.* recently reported that ITO NC doping concentration and size affect the electrochemical modulation of infrared absorbance with the nature and extent of modulation being strongly influenced by surface depletion effects.²⁸ The authors concluded that large-sized, low-doped ITO NCs are expected to show lower optical modulation and retain high transparency in the visible to near-infrared region at all electrochemical states of charge. In the present context, the selection of large-sized, low-doped ITO NCs minimizes RI modulation of ITO NCs, so that dynamic control of the Bragg stacks is expected to be dictated by the modulation of properties of the WO_{3-x} NC layers. Based on the above rationale, 15 nm diameter 0.4 at% ITO and 5 nm WO_{3-x} NCs were synthesized by modifications of previous processes using slow growth and hot injection methods, respectively.^{29,34} (Figure B.3 in Appendix B)

3.3.2 Film processing: ligand-capped versus ligand-stripped NCs

As-synthesized NCs are capped with native organic ligands preventing NC agglomeration and helping control growth kinetics during colloidal synthesis.³⁵ However, in electronic or electrochemical devices, capping ligands act as an insulating barrier that needs to be removed to lower the barrier to electron transport through NC films.³⁶ NC films can be annealed at high temperature to remove organic ligands or ligands can also be removed chemically either before or after film deposition.^{25,37} The former strategy usually results in higher porosity (Figure B.5 in Appendix B). In our case, those pores are filled

with electrolytes (RI~1.5), lowering the effective RI of layer and also lowering the RI contrast between layers, which decreases the Bragg reflectance.¹⁸ So, in order to maximize RI contrast, all the Bragg stack films in our experiments were spin-coated from dispersions of NCs that had been ligand-stripped and were dispersed in a dimethylformamide (DMF) and acetonitrile (ACN) mixture. The high volatility of ACN leads to thicker, uniform NC films than could be achieved from DMF alone. Following the previous methods for ligand removal, Meerwein's salt in ACN and NOBF₄ in DMF were used to remove ligands from WO_{3-x} and ITO NCs, respectively.^{38,39} Optimization of film processing methodology was crucial to produce consistent and reproducible NC film stacks for the development of high optical quality photonic architectures.

3.3.3 Optical properties of NC films

Accurately knowing the RI of each layer is highly important to predict the optical properties of Bragg stacks. Given geometric parameters, like thickness of each NC layer and the number of bilayers, as well as the optical constants of each NC layer at different electrochemical state of charge, the optical performance of the Bragg stack using the transfer matrix method was predicted and optimized.^{40,41} Ellipsometry with an in situ electrochemical liquid cell was employed to track the dynamic change of effective optical properties (n and k) of NC films, including the incorporated electrolyte, as a function of charging potential (Figure 3.1a). This in situ monitoring allows us to precisely know the relevant optical properties, avoiding changes during sample transfer that may compromise ex situ measurements. The NC film acts as the working electrode, Li metal is the reference and counter electrode, and 1 M LiTFSI in tetraglyme is the electrolyte solution in the

experimental electrochemical setup, the same configuration that is used to study optical modulation of Bragg stacks (vide infra).

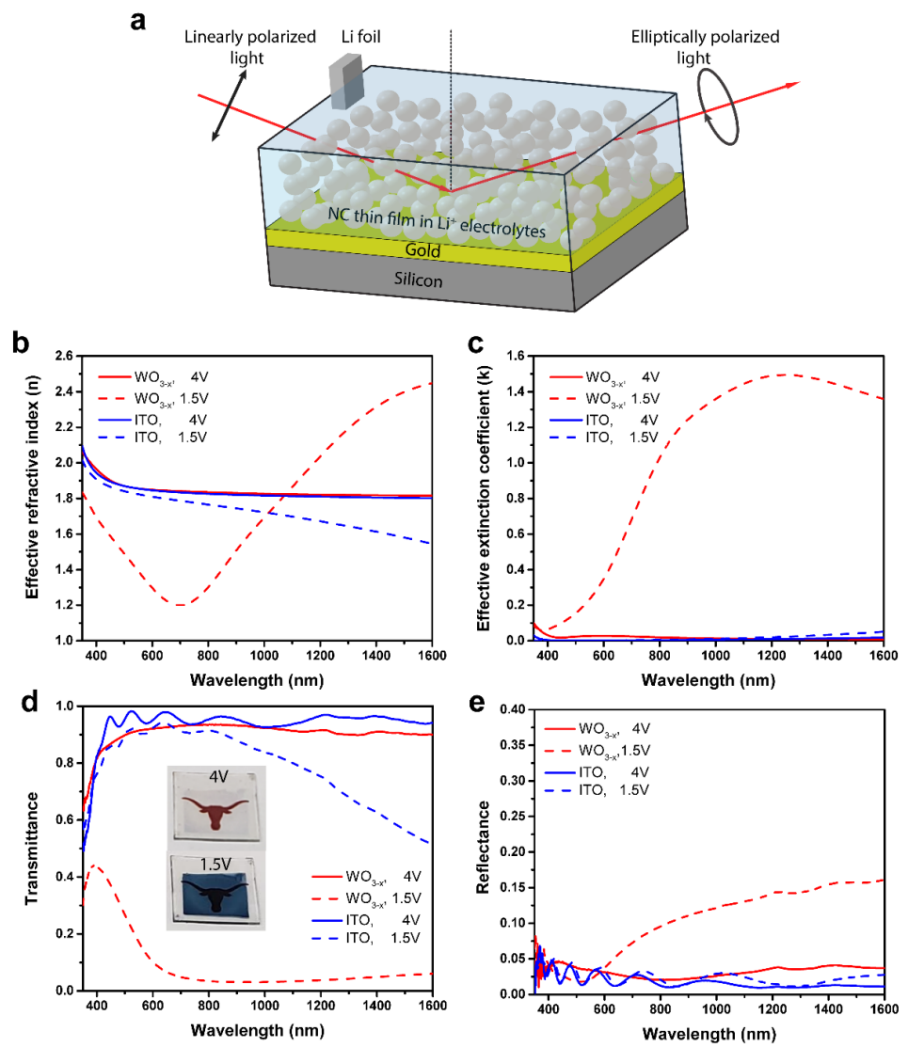


Figure 3.1 Optical characterization of ITO and WO_{3-x} NC films. (a) Illustration of *in situ* electrochemical ellipsometry measurement. (b,c) Effective refractive index and extinction coefficients of NC thin films immersed in electrolytes at 4 V and 1.5 V (vs Li/Li^+). (d,e) *In situ* transmittance and reflectance of 220 nm-thick WO_{3-x} and 680 nm-thick ITO NC films

measured at 30° angle of incidence (AOI). These samples were annealed at 300°C at the final step.

Considering the degree of optical modulation depends on the applied potential, we measured optical constants at various potentials. The effective complex RI ($\tilde{n} = n + ik$) of the NC films incorporating the electrolyte were obtained by fitting psi and delta values measured by in situ ellipsometry at different states of charge. Obtained optical constants of 300°C annealed films at each potential from 4 V to 1.5 V with 500 mV steps are summarized in Figure B.8 in Appendix B. The derived optical constants (Figure 3.1b,c and Figure B.8 in Appendix B) as well as original psi and delta values (Figure B.7 in Appendix B) show that in the visible to near-infrared spectral range, the change in optical constants of ITO films is minimal while optical constants of WO_{3-x} films have a strong dependence on the state of charge. We also assessed the reflection and transmission modulation of metal oxide NC films coated onto ITO-coated glass, which itself was transparent in the visible and near-infrared. Corroborating our observations using ellipsometry, very little modulation of reflection and transmission was observed for an ITO NC film between the charged state at 1.5 V and bleached state at 4 V, even when the thickness ITO NC film was as high as 680 nm. The low modulation can be attributed to: 1) the low tin doping concentration shifts the LSPR of ITO NC to the mid-infrared region (Figure B.4 in Appendix B), 2) Li ions do not intercalate into the ITO crystal lattice, so electrochemical charging of ITO NC film happens through a capacitive charge compensation process. Zandi *et al.* established that for larger NCs, the modulation of LSPR frequency is minimal due to

little change in the electron concentration in the non-depleted NC core during modulation.²⁸

Only a slight increase in near-infrared absorption was observed for a thick ITO NC film.

In contrast to ITO NCs, there is huge change of effective RI modulation of WO_{3-x} NC films. Electrochemical lithiation of WO_{3-x} modifies electronic properties including the free carrier concentration and effective mass thereby substantially modifying the optical constants. These changes induce a strong optical modulation as shown in the Figure 3.1d. Interestingly, lithiated WO_{3-x} NC films also had substantial reflectance in the visible and near-infrared range, consistent with a high concentration of mobile electrons (Figure 3.1e).

The photonic reflection and transmission characteristics of the Bragg stack is determined by the RI contrast between WO_{3-x} and ITO NC films. As seen in Figure 3.1b, the effective RI of WO_{3-x} and ITO NC layers at 4 V were very similar such that reflectance would be minimized in both the visible and near-infrared. Considering that the bulk RI of ITO (2.19) is larger than that of WO_{3-x} (2.1), the NC film morphology plays an important role. The larger ITO NCs result in greater RI reduction compared to the bulk, bringing the effective RI of the two NC films very close in the transparent state. On the other hand, the RI contrast between the two NC layers in the charged state is substantial, providing ample opportunity to design modurable Bragg stacks.

3.3.4 Simulation using transfer matrix method

The design parameters determining the optical properties of Bragg stacks made of ITO and WO_{3-x} NC films are 1) thickness of ITO and WO_{3-x} NC layers, 2) number of unit cells, and 3) RI contrast between ITO and WO_{3-x} NC layers. Given the geometric and RI information at different states of charge, the transfer matrix method was applied to predict

the optical properties of the Bragg stack as a function of different geometric parameters such as relative thickness and the number of unit cells. The model includes the alternating layers of WO_{3-x} and ITO NCs deposited on ITO-coated glass and immersed in 1 M LiTFSI in tetraglyme electrolyte, same as used for experimental observations described below (Figure 3.2a).

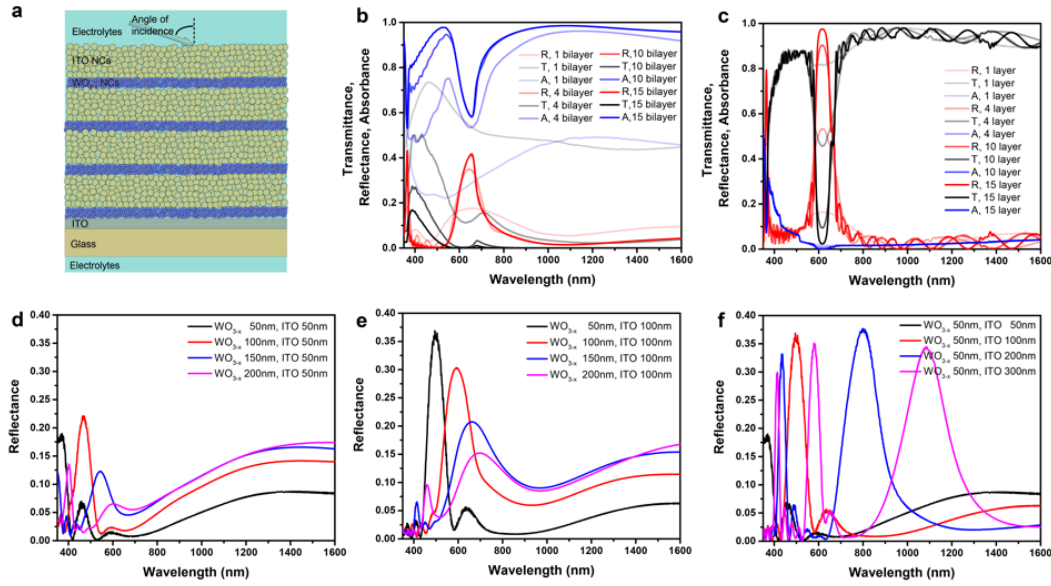


Figure 3.2 Simulated optical spectra of Bragg stacks charged at 1.5 V using the transfer matrix method. (a) Schematic stack employed to simulate reflectance, transmittance, and absorbance. (b) Simulated optical spectra of charged Bragg stacks for different numbers of bilayers (150 nm ITO/ 50 nm WO_{3-x}) at 30° angle of incidence using optical constants from *in situ* ellipsometry. (c) Simulated optical spectra with same conditions as (b) except assuming no absorption by the NC layers. (d,e,f) Effect of NC layer thickness on reflectance of charged Bragg stacks with 4 bilayers.

The width and position of the photonic stop band in any Bragg stack is mainly determined by the RI contrast and relative thickness of the constituent layers in the unit cell. Given the unit cell, the intensity depends on the number of unit cells. Here, characteristics of the photonic stop band of Bragg stacks were simulated where the unit cell is composed of one ITO and one WO_{3-x} NC film. First, the effect of the number of bilayers was simulated by fixing the WO_{3-x} and ITO layer thicknesses as 150 nm and 50 nm, respectively. As the number of bilayers increases from 1 to 15 bilayers, the reflectance in the charged state at 1.5 V increases but ultimately limited to 40% due to strong absorption by lithiated WO_{3-x} NCs (Figure 3.2b). For this reason, the reflection in our case does not increase with the number of layers, contrary to the previous reports based on dielectric materials.^{42,43} Because our simulations use the complex RI as input, this important, limiting effect of the extinction coefficient causing absorption is predicted.

Meanwhile, due to the combination of Bragg reflection and the strong absorption of charged WO_{3-x} NCs, strong transmittance modulation is predicted. Reflectance increases as the number of layer increases if no absorption in the Bragg stack layers is assumed (Figure 3.2c). From these simulations, our conclusion is strong absorption is beneficial for large transmittance modulation, but it limits the potential reflectance. Since there is small difference in reflectance between 4 and 10 bilayers, we simulated varying the thicknesses of WO_{3-x} and ITO NC layers while fixing the number of bilayers at 4. Increasing the WO_{3-x} thickness red-shifted and broadened the photonic bandwidth and led to broad reflectance arising from the WO_{3-x} reflection in the near-infrared range (Figure 3.2d,e). Tuning of the

peak reflectance ranging from the visible to near-infrared was achieved by setting the WO_{3-x} thickness at 50 nm and increasing the ITO thickness, red-shifting the maximum peak position while maintaining the peak reflectance (Figure 3.2f). The non-dispersive optical behavior of LSPR active NCs means the Bragg stack reflectance does not follow simple a Bragg's law equation for the peak wavelength that might be valid for dielectric materials, i.e., $2(n_L d_L \cos q_L + n_H d_H \cos q_H) = m\lambda_m$, where m is diffraction order, λ_m is maximum peak wavelength, n_L and n_H are the low and high RI, d_L and d_H are the thickness of each layer, and q_L and q_H are the incidence angles of light from low RI layer to high RI layer, and vice versa. For example, for a 50 nm WO_{3-x}/ 300 nm ITO Bragg stack, the first (1085 nm), second (580 nm), and third (415 nm) order reflectance peaks do not follow an integer multiple sequence (Figure 3.2f). This deviation underscores the importance of the transfer matrix simulations since even basic characteristics could not be easily predicted with simple calculations. The use of complex RI including extinction coefficient (k) endows the more complex spectral characteristics of the Bragg peaks. In addition to the reflection owing to photonic effects, the increase in carrier density in the WO_{3-x} NCs at 1.5 V results in increase of LSPR absorption. As a result, the overall transmittance ($T=1-R-A$) of the charged Bragg stack approaches zero in the colored state. The simultaneous modulation of reflection and absorption leads to large optical modulation between the bleached and transparent optical states.

3.3.5 In situ measurement of Bragg stack modulation

Based on our simulation results (Figure 3.2f), Bragg stacks on ITO-coated glass substrates were fabricated. In order to tune the reflectance in the visible and near-infrared

range, the ITO layer thickness (125 nm, 165 nm, and 330 nm) was varied while setting the thickness of the WO_{3-x} layers as 55 nm. As the realization of a photonic stop band requires precise control of each layer, the fabrication process was challenging. The optimization of film deposition parameters plays a crucial role in fabricating Bragg stacks with spatially uniform and predictable optical characteristics. In order to vary the thickness of the ITO layers while consistently producing uniform films, the NC concentration in the dispersion was changed. After each spin-coating of the dispersion, annealing on a hot plate for 5 min at 250°C was used to enhance the physical bonding between NCs and prevent the dissolution of NCs during deposition of subsequent layers. After the final layer was added, Bragg stacks were baked at 300°C for 30 min. ITO thicknesses of 165 nm and 125 nm with 4 bilayers were well-suited for visible reflection while ITO layers of 330 nm-thick with 3 bilayers was evaluated for near-infrared and visible reflection. As shown in Figure 3.3 and Figure B.11 in Appendix B, films were crack-free and uniform without haziness, making them suitable for optical coatings. Therefore, diffuse reflectance was ruled out as a contribution to the measured optical properties.

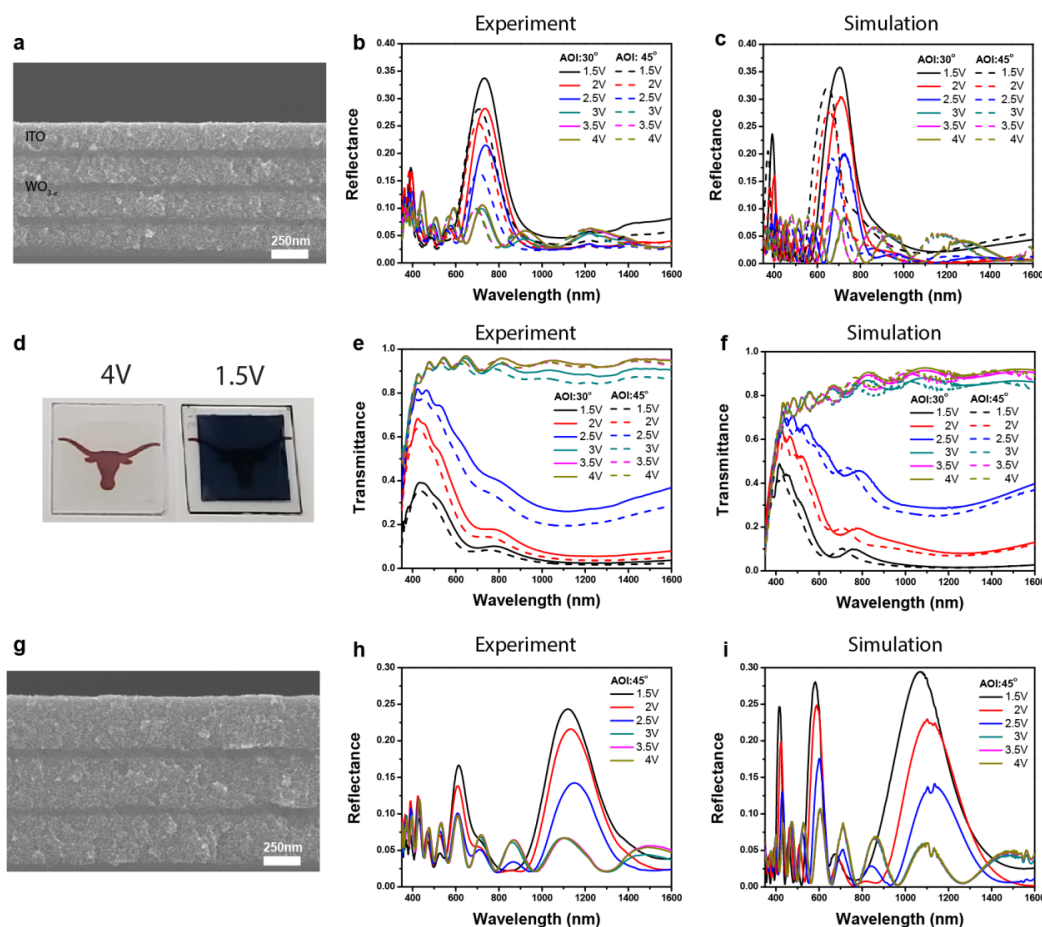


Figure 3.3 Optical modulation of Bragg stacks. (a,g) Cross-sectional SEM images of Bragg stacks consisting of 165 nm ITO/ 55 nm WO_{3-x} NC layers with 4 bilayers (BS1) and 330 nm ITO/ 55 nm WO_{3-x} NC layers with 3 bilayers (BS3), respectively. (d) Pictures of a Bragg stack with the structure shown in (a) on an ITO-coated glass substrate charged at 1.5 V and discharged at 4 V. (b,e) *In situ* experimental and (c,f) simulated spectra of reflectance and transmittance of sample (a). (h,i) Experimental and simulated spectra of reflectance and transmittance of sample (g). These Bragg samples were baked at 300°C at the final step.

In our experiments, transmittance and reflectance were measured in situ using our home-built spectroelectrochemistry setup where a Bragg stack film on an ITO substrate acts as the working electrode immersed in 1 M LiTFSI in tetraglyme electrolyte with lithium foil as the reference and counter electrodes. The working electrode was illuminated at different angles of incidence (AOI, near 0°, 30°, and 45°) with white unpolarized light and transmitted as well as reflected light was collected at different applied potentials ranging from 4 V to 1.5 V at a step size of 500 mV. The Bragg stack of 4 unit cells of 165 nm-thick ITO NC films and 55 nm-thick WO_{3-x} NC films (BS1) displays a reflectance band in the 700-800 nm wavelength range. BS1 exhibits a reflectance maximum at 750 nm at 30° AOI covering the visible and near-infrared range (Figure 3.3b). Changing the applied potential from oxidizing 4 V to reducing 1.5 V, the maximum reflectance shifted from 10 to 34%. The experimental BS1 reflection is well matched with the predicted spectral response using the model described above (Figure 3.3c). As expected, in the visible to near-infrared spectrum, the modulation of WO_{3-x} film RI mainly dictates reflectance. Notably, the reflectance increases below 3 V, corresponding with 1) the change of RI of WO_{3-x} NC films starting from 3 V (Figure B.8 in Appendix B) and 2) a significant increase in the charging current of WO_{3-x} films starting from 3 V in cyclic voltammetry (Figure B.6 in Appendix B). As the applying potential decreased from 3 V to 1.5 V, reflectance increased and slightly blue-shifted. Transmittance measurements further confirmed the reflected Bragg peaks. The reflectance band is spectrally matched with a broad hump in the transmittance spectra (Figure 3.3e), which is clearly different with the spectra of WO_{3-x} NCs alone (Figure 3.1d).

The reflectance decreases and blue-shifts, showing an iridescent character when the AOI increases from 30° to 45°. The lower transmittance at higher AOI can be explained based on the increased optical path length. When the films were discharged at 4 V, the reflectance was below 10%, leading to high transmittance state ('off' reflectance). Electrochemical switching was rapid, despite the porosity of WO_{3-x} NC films being limited to as little as 5%, with the optical change reaching 90% of its maximum within one minute. When the thickness of ITO NC layer in the unit cell was decreased to 125 nm (BS2) from 165 nm (BS1), the reflectance band moved toward higher energy (550 nm) while the maximum reflectance decreased at all applied potential (Figure B.13 in Appendix B). When the thickness of ITO NC layers in the unit cell was increased to 330 nm-thick while setting the thickness of WO_{3-x} layers fixed at 55 nm (BS3), the primary reflectance band shifted to the infrared (1100 nm). In BS3 (Figure 3.3g), a strong second order peak was apparent in the visible spectrum at 600 nm (Figure 3.3h,i). Overall, experimental data follows similar trends as the simulated spectra, supporting the efficacy of using optical simulations to design tunable Bragg stacks so long as the fabrication approach enables precision. Specifically in this case, Bragg stacks with tunable photonic band gaps from the visible to infrared spectrum were demonstrated.

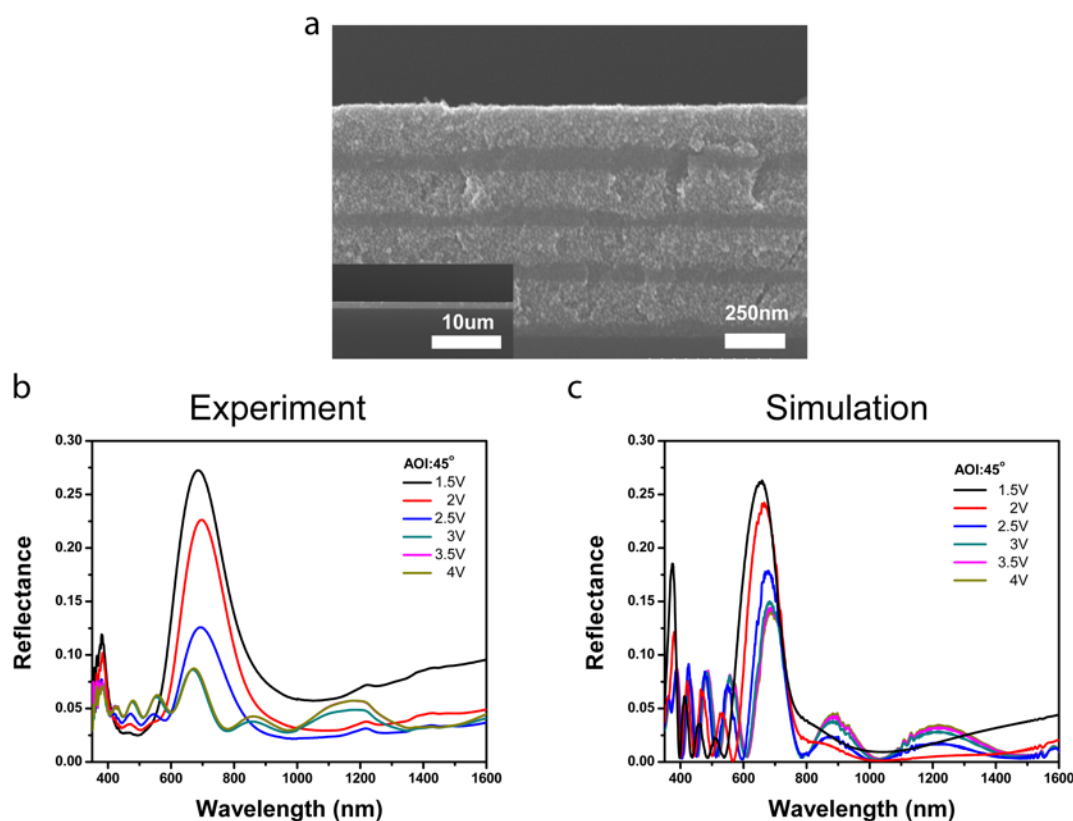


Figure 3.4 Bragg stacks with no annealing process. (a) SEM cross-section images of Bragg stacks consisting of 170 nm ITO/ 60 nm WO_{3-x} with 4 bilayers (BS4) (b,c) Simulated and experimental spectra of reflectance and transmittance of sample (a) fabricated on ITO-coated glass substrates. The final annealing temperature for this sample was limited to 150°C on hotplate.

Bragg reflection, in combination with electrochemically induced absorption, can also be used to tune the color of electrochromic windows. Comparing the charged WO_{3-x} NC-only and the charged Bragg stack films (Figure 3.1d and Figure 3.3d,e, respectively), the color is affected by Bragg reflectance, while absorption by the ITO NCs does not

significantly impact visible coloration. In prior work, combination of different materials is mostly tried, e.g., WO_x - NbO_x composites, to tune color.^{29,43,44} Color indices in the CIELab space evaluated by D50 illuminant give quantifiable colorimetry information in which higher L^* (0-100) indicates lightness, a^* represents green ($-a^*$) to red (a^*), and b^* represents blue ($-b^*$) to yellow (b^*). In our work, based on the contributions of interband absorption of ITO NCs and Bragg reflection, as well as the strong absorption of lithiated WO_{3-x} NCs, transmitted color is varied. The tunable position of Bragg reflection affects light in the red region whereas interband absorption of ITO NC thin films absorbs the bluer light. As an example, because BS2 (125 nm ITO/ 55 nm WO_{3-x} with 4 bilayers) shows Bragg reflection at shorter wavelength than BS1 (165 nm ITO/ 55 nm WO_{3-x} with 4 bilayer films), BS2 ($L^* = 62$, $a^* = -5$, $b^* = -36$) is less green (more reddish) than BS1 ($L^* = 65$, $a^* = -14$, $b^* = -25$). (Figure B.12 in Appendix B)

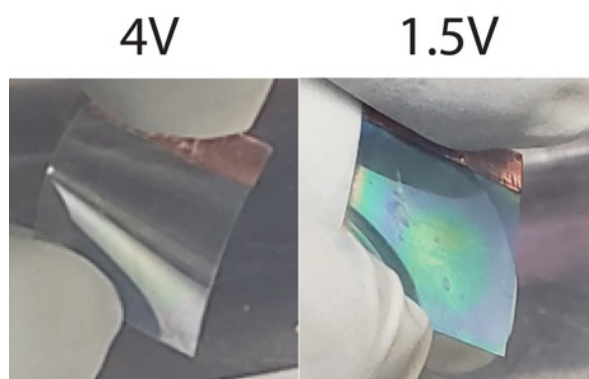


Figure 3.5 Optical photograph of charged and discharged Bragg stack (BS5) on ITO-coated PET.

Fabrication of Bragg stacks on flexible substrates was possible using ligand-stripped NCs as building blocks. We figured out ligand-stripped NCs can be continuously layer-by-layer deposited without employing the soft bake annealing process. On the other hand, when ligand-capped NCs were coated in multiple layers, subsequent deposition processes severely disrupted as-deposited NC film, effectively washing away the NCs. We assume that deposited ligand-stripped NCs are effectively kinetically trapped, which allows coating NCs layer-by-layer without any high temperature annealing processes ($>200\text{ }^{\circ}\text{C}$) substrates. Using this method, Bragg stack on both ITO-coated glass substrates (BS4) was fabricated and performance was measured, and also demonstrated Bragg stack on ITO-coated flexible polyethylene terephthalate (PET) substrates (BS5). As can be seen in the Figure 3.4a, BS4 shows no significant crack over a large area and also exhibited strong modulation of reflectance, predicted by simulation (Figure 3.4b,c). However, it should be mentioned that the interfaces between the layers are not as smooth as BS1,2,3, demonstrating that the soft baking used in those samples between each deposition step was helpful in forming distinct boundaries between layers. Interfacial roughness can also make the predictability based on simulation more challenging. Moreover, the maximum reflectance (27%) is limited compared to 300°C annealed films (34%), ascribed mostly to the reduced optical modulation of WO_{3-x} films that have undergone high temperature annealing (Figure B.1 and B.10 in Appendix B). Similar to BS4, BS5 was fabricated on a flexible ITO-coated PET substrate and also shows switchable reflectance in the visible region between colored state charged at 1.5 V and the transparent state discharged at 4V (Figure 3.5).

3.4 CONCLUSION

In summary, doped semiconductor NCs can be effectively used to fabricating optimized tunable Bragg stacks for electrochromic windows. LSPR active ITO NC and WO_{3-x} NC as our constituent materials were judiciously selected from precisely tuned NCs with a mechanistic understanding of their optical modulation behavior. In situ ellipsometry was used to measure and analyze the RI of ITO NC films and WO_{3-x} NC films at different electrochemical states of charge. Using the experimentally determined RI data from in situ ellipsometry, the optical properties of tunable Bragg stacks were predicted and optimized using the transfer matrix theoretical model. Based on the predictions from the theoretical model, Bragg stacks with strong ‘on and off’ reflection modulation was realized that varied from the visible to near-infrared. Furthermore, we demonstrated NC-based Bragg stacks which can be fabricated on flexible PET substrates. The strategy used here could be applied to achieve other targeted dynamic properties over a broad wavelength range. The resulting Bragg stacks could be customized for potential applications such as electrochromic smart windows, dynamic optical filters, and reflective coatings.

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Chapter 4: Cation-dependent Spectroelectrochemical Properties of Plasmonic Tungsten Oxide Nanocrystals

4.1 INTRODUCTION

Dynamic spectroelectrochemical modulation from plasmonic metal oxide nanocrystals (NCs) is promising for advanced electrochromic devices.¹⁻⁴ High carrier concentration given by electrochemical charging or synthetic doping as well as nanosized domain provide interesting spectroelectrochemical properties. Owing to its inherent porous nature from loose packing of NCs and high surface-to-volume ratio, kinetics can be increased from reduced diffusion length and increased capacitive charging contribution compared to the bulk thin films fabricated by vacuum deposition process.⁵⁻⁶ Moreover, adjustable high concentration of free carriers delocalized over entire NCs give dynamic localized surface plasmon resonance (LSPR) properties in the near-infrared region which is also hard to achieve from conventional electrochromic materials.⁷⁻⁹ This plasmon-induced near-infrared absorption properties widened the scope of modulation property of smart windows.

Most widely known dynamic plasmonic metal oxide material is indium tin oxide (ITO) NCs showing dynamic LSPR modulation in the near-infrared range from double-layer capacitive charging kinetics.¹⁰⁻¹¹ In this case, ions cannot intercalate into the structure within potential range from 4 V to 1.5 V vs Li/Li⁺. If ion intercalation is involved, more diverse absorption properties can be evolved. In case of Nb-doped TiO₂ NC thin films, independent optical modulation of polaronic and plasmonic absorption in the visible and

near-infrared region has been observed attributed to different mechanisms of intercalation and capacitive charging, respectively which is not attainable from non-intercalating bulky ions.^{1,12} As such, doped metal oxide NCs having lower energetic barrier to ion diffusion will allow ions to diffuse into the structure, enriching spectroelectrochemical properties.

Above mentioned advantage of plasmonic semiconductor NCs can be a way of overcoming limitation of alternative electrolytes system to typical lithium (Li^+) electrolytes. Most of all, sodium ion (Na^+)-based electrochemical system has been extensively paid attention in recent years as an alternative to the Li^+ mainly from its earth abundant nature.¹³⁻¹⁶ For the same reason, Na^+ electrolytes system is promising for electrochromic windows considering rapid growth of market and large scale installation of windows.^{17,18} However, the radius of Na^+ (102 pm) is 34 % bigger than that of Li^+ (76 pm), making big difference in kinetics and thermodynamic behavior as demonstrated from the battery research.¹⁹⁻²⁰ Dini *et al.* observed slow insertion kinetics and low optical modulation for Na^+ -based electrochromism on amorphous tungsten trioxide thin films mainly because of its large ionic size.²¹ Despite strong advantage of cost effectiveness, there are few reports of Na^+ -based electrochromic studies because of its slow kinetics.²²⁻²⁴ This limitation can be possibly improved by using nanostructured plasmonic metal oxide thin films with considering crystal structure of ion diffusion channels.

Among different doped metal oxide NCs for electrochromic materials, tungsten suboxide is obviously best candidate because of its strong absorption in the visible and near-infrared region which can block large portion of solar transmittance.²⁵⁻²⁷ It has perovskite structure while missing A site. As oxygen-deficiency increases, the structure

changes to different crystal phase by creating shear plane, so-called crystal shear mechanism.²⁸ Depending on the degree of oxygen vacancy, different packing of WO₆ octahedra such as corner-sharing and edge-sharing along a- and c- directions creates different crystal phase with different tunnel sites such as trigonal cavity, hexagonal tunnel, and square windows. For instance, monoclinic WO₃ phase has only square windows while monoclinic WO_{2.72} (m-WO_{2.72}) has different size of tunnel sites. These void spaces are wide enough to allow lithium ion diffusion but having different energy barrier for ion diffusion. But some of the site such as trigonal cavity is too narrow to incorporate larger size of ions such as Na⁺ and K⁺. As ions diffuse through those tunnel sites, different spectroelectrochemical properties are expected for different size of ion intercalation. Moreover, the degree of oxygen vacancy affects electronic conductivity related to the switching kinetics.²⁹ As the degree of oxygen vacancy affects important parameters in electrochromic performance, judicious selection of NCs is required.

Another advantage of colloiddally synthesized doped metal oxide NCs is precise control of size, doping ratio, phase, and the shape which are prerequisite for understanding ion intercalation in crystal structure and its relation to spectroelectrochemical properties. However, these studies are at the early stage despite its importance. Part of the reason is processed film has different state with NCs dispersed in solution. Thermal annealing process usually employed to remove insulating ligands induces oxygen incorporation into the NCs, which is especially critical for tungsten oxide NCs where the phase change depends on the degree of oxygen vacancy. Electrochemical stability also needs to be guaranteed during electrochemical measurements. In order to study more precisely, both

condition of preventing severe degradation and retaining NCs properties in the film are necessary.

4.2 METHODS

4.2.1 Materials

Tungsten hexacarbonyl ($W(CO)_6$, 99.9%) was purchased from Stem chemical. Trimethylamine N-oxide (Me_3NO , 98%), triethyloxonium tetrafluoroborate (Et_3OBF_4 , 97%), acetonitrile (ACN, anhydrous, 99.8%), *N,N*-dimethylformamide (DMF, anhydrous, 99.8%), toluene (anhydrous, 99.8%), oleylamine (technical grade, 70%), 2-propanol (IPA, anhydrous, 99.5%) were purchased from Sigma-Aldrich.

4.2.2 Synthesis of monoclinic $WO_{2.72}$ nanorods

0.7 g of $W(CO)_6$ and 1.33g of Me_3NO were dissolved in the 5.35 g of oleylamine inside a N_2 glovebox. The solvent mixture is directly heated to 300°C and kept for 1h 30 min. After the reaction was done, solutions were transferred into the glovebox, washed with IPA, and redispersed in the toluene, which was repeated for 2 times, each time centrifuging to collect the flocculated nanocrystals.

4.2.3 Ligand stripping of $WO_{2.72}$ nanorods and film processing

Ligand stripping process was done by following previously reported procedure. Briefly, Et_3OBF_4 in ACN (30mg/ml) was mixed with NCs dispersed in the toluene (10mg/ml). After the stripping, the NCs were washed using toluene and DMF as antisolvent and solvent, respectively. Stripped nanorods dispersed in the ACN/DMF mixture (6:4) (80mg/ml) were spin-coated to make uniform films.

4.2.4 Al₂O₃ atomic layer deposition

ALD was processed using Cambridge Nanotech Savannah S100 atomic layer deposition chamber. Films were heated to 180°C for 10 minutes at a pressure of 0.5 Torr under nitrogen flow. Typical growth rate of Al₂O₃ is 1.1 Å per cycle. Each cycle composed of 0.1s pulse of trimethylaluminum (TMA), a 30s purge, a 0.1s pulse of water, and a 30s purge.

4.2.5 SEM and STEM measurement

Hitachi S-5500 was used for characterizing the morphology of m-WO_{2.72} thin films before and after Al₂O₃ ALD. STEM mode was used to image the morphology and the size of nanorods.

4.2.6 *In situ* spectroelectrochemical measurement

The measurement was done using home-built spectroelectrochemistry setup. Our samples were immersed in the electrolytes system (0.5 M LiClO₄ in tetraglyme or 0.5 M NaClO₄ in tetraglyme) with Li foil or Na foil as a reference electrode. For the TBA⁺ experiments, Ag/AgNO₃ used as pseudo-reference electrode and Pt was used as counter electrode.

4.2.7 TOF-SIMS measurement

For the sample preparation, after 30 cycling of bare and 1nm Al₂O₃ deposited m-WO_{2.72} films on highly doped silicon substrates with chronoamperometric cycling, both samples were rinsed with dimethyl carbonate using same washing process and transferred to the air-free interface (U.S. Patent Application Serial No. 14/445,650 filed 29 July 2014). A TOF SIMS 5 spectrometer (ION-TOF GmbH) was used with ultra-high vacuum

condition at pressure below 2×10^{-9} mbar. All detected secondary ions of interest had a mass resolution $> 5,000$ and possessed negative polarity. A pulsed 30keV Bi¹⁺ (20ms) ion beam set in either the High Current mode or Burst Alignment mode (with seven bursts) was applied for depth profiling.

4.2.8 XPS measurement

X-ray photoelectron spectroscopy (XPS) measurements of bare, 1nm, and 2nm ALD samples were done on Kratos X-ray photoelectron spectrometer – axis ultra DLD using aluminum K-alpha source. Data was calibrated to the C 1s peak at 284.8 eV from adventitious carbon and analysis was done using CasaXPS software.

4.3 RESULTS AND DISCUSSION

As a model system, we synthesized m-WO_{2.72} nanorods for studying spectroelectrochemical properties of different size of cation intercalation into the crystal structure (Figure 4.1 c). This nanorod has narrow width (7.0 ± 1.1 nm) and nanoscale length (75.5 ± 15.2 nm), so diffusion length is small (Figure 4.1 a). More importantly, the structure has hexagonal tunnel through b-axis which makes this crystal phase interesting. Hexagonal phase tungsten oxide has been noted from its large void space of hexagonal tunnel. This has shown enhanced proton transport properties as well as pseudocapacitive behavior.³⁰⁻³¹ Owing to structural similarity to hexagonal tungsten oxide having large hexagonal tunnels (H), square windows (S), and trigonal cavity (T), m-WO_{2.72} nanorods were selected (Figure 4.1 d). This different size of void space can be selective to different size of ion intercalation,

impacting spectroelectrochemical properties. We hypothesized sodium ions are too large to fit in the trigonal cavity different with lithium ion which are known to occupy this site, so they will show different spectroelectrochemical properties.³²⁻³⁴ Moreover, from nanostructuring and intracrystalline hexagonal tunnel sites, kinetic and modulation properties of Na^+ can also be increased.

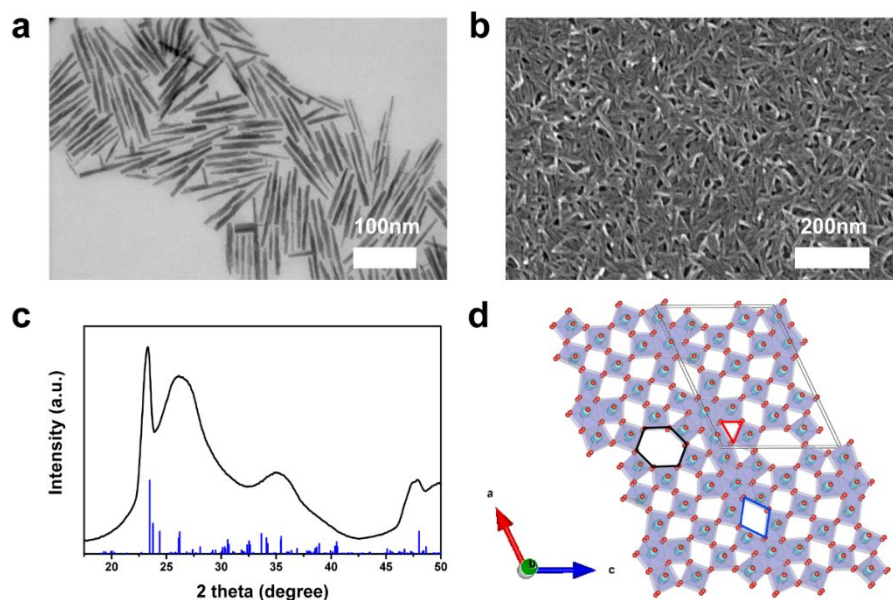


Figure 4.1 Structural aspects of $\text{m-WO}_{2.72}$ nanorods. (a) STEM image of nanorods (b) SEM image of porous nanorod films coated with 1nm Al_2O_3 from ALD. (c) XRD pattern of nanorods prepared by drop-casting and reference $\text{m-WO}_{2.72}$ pattern (ICSD code #15254). (d) $\text{m-WO}_{2.72}$ crystal structure having hexagonal tunnel (black), trigonal cavity (red), and square window (blue).

In order to study different cation intercalation effect on spectroelectrochemistry related to crystal structure, we needed to preserve the crystal phase in the assembled films as well as have high porosity for fast kinetics which is hard to achieve both condition from typical approach of annealing process to remove organic ligands. In our previous study, we fabricated porous thin films by using electrostatic repulsion between nanorods from solution phase ligand-stripping strategy.²⁶ Following this work, porous thin film was fabricated from spin-coating process with preserving crystal phase of m-WO_{2.72}. (Figure C.1 and C.2 in Appendix C). Fabricated films still have strong absorption in the visible and near-infrared region, confirming the plasmonic NC optical properties are preserved (Figure 4.2e and Figure C.3 in Appendix C).

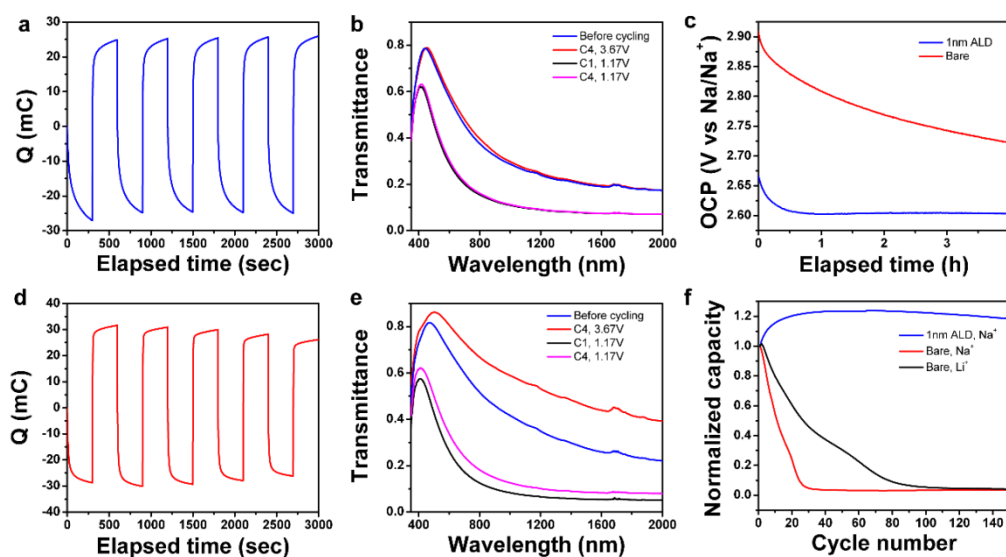


Figure 4.2 Spectroelectrochemical property of bare and 1 nm Al₂O₃ layer coated m-WO_{2.72} film. Chronoamperometric cycling between 3.67 V to 1.17 V of 1 nm Al₂O₃-coated (a) and bare m-WO_{2.72} (d) film. Transmittance spectra of 1 nm Al₂O₃-coated (b) and bare (e) m-

WO_{2.72} film. (c) Open circuit potential (OCP) of bare and 1 nm Al₂O₃-coated m-WO_{2.72} film immersed in 0.5 M NaClO₄ in propylene carbonate electrolytes. (f) Cycling test of bare and 1 nm Al₂O₃-coated m-WO_{2.72} film with Na⁺ electrolytes and bare m-WO_{2.72} film with Li⁺ electrolytes.

Initially, as-deposited m-WO_{2.72} nanorods films were tested in the 0.5 M NaClO₄ in propylene carbonate electrolytes. However, after several electrochemical cycling, capacity and optical properties degrade fast (Figure 4.2 d,e,f). We suspected the electrolytes decomposition on the NC surface is the major source of degradation considering continuous open circuit potential degrade of bare films upon electrolytes immersion (Figure 4.2 c). Similar observation of solid electrolyte interphase (SEI) formation was demonstrated in LiMn₂O₄ thin films immediately after electrolytes exposure.³⁵ Even though NCs enhance the ion diffusion kinetics, increased surface area often increases the surface reaction with electrolytes. This high surface area of NCs have been problem of NC application to battery due to the enhanced SEI formation which blocks the efficient ion transport.³⁶ Electrolytes degradation in electrochromic application is more related to the material property considering applying potential window is usually moderate compared to battery operation. In fact, ITO NC thin films exhibited pretty robust cycling stability, showing our high degree of oxygen deficient m-WO_{2.72} nanorods are more catalytically active.³⁷ The degradation is especially severe in Na⁺ system compared to the Li⁺ electrolytes system.

Meanwhile, alumina (Al_2O_3) ALD has proven to prevent severe electrolytes decomposition and mechanical delamination.³⁸⁻⁴² It has been reported that Na^+ diffusion is efficient in Al_2O_3 layer.⁴⁰ Other than this role, Al_2O_3 ALD can also be beneficial for preventing photochromic effect in electrochromic applications. Yang *et al.* employed Ta_2O_5 layer from ALD as a hole-blocking layer demonstrating reduced photochromic side effect.⁴³ Larger band gap of Al_2O_3 can efficiently block the hole transfer to the electrolytes. Al_2O_3 is also optically passive, allowing us to study modulation properties of tungsten oxide materials. Motivated from above reasons, we employed Al_2O_3 ALD in our porous m- $\text{WO}_{2.72}$ mesoporous thin films. As shown in the XPS measurements (Figure C.4 in Appendix C), peak originated from Al become more intense as alumina layer increases demonstrating successful Al_2O_3 ALD. TOF-SIMS analysis also confirmed Al_2O_3 is deposited throughout the entire depth of NC films. (Figure C.7 in Appendix C) It should be mentioned the crystal phase of m- $\text{WO}_{2.72}$ was retained even after the Al_2O_3 deposition (Figure C.1 in Appendix C).

1 nm ALD gives stabilized OCP and cycling stability, confirming the effective passivation of m- $\text{WO}_{2.72}$ (Figure 4.2 c,f). At the first cycling of 1 nm Al_2O_3 ALD films, capacity didn't recover to initial state, meaning the activation of Al-O-Na bonding as reported in a previous paper.³⁹ As shown in Figure 4.2 b,e, the passivation strategy also prevents severe optical property change different with cycling of bare films. Capacity gradually increased at 2 nm Al_2O_3 ALD (Figure C.5 in Appendix C).

Major sources of significant degradation of bare films can be from either NCs delamination or electrolytes degradation. First factor of NCs delamination was removed by

checking the cross-section SEM measurement of 400 cycled bare and 1 nm Al_2O_3 -coated films. As shown in Figure C.6 in Appendix C, the film thickness is almost same which cannot explain the significant capacity degradation. The part of the reason can be most of charging is from capacitive charging than intercalative charging, thus giving less strain to the nanocrystal structure. In order to prove electrolytes decomposition is the main source of stability degrade, TOF-SIMS analysis is employed for 30 cycled bare and 1 nm Al_2O_3 deposited films (Figure C.7 in Appendix C). This technique has been employed to detect SEI species in battery research owing to its very high chemical selectivity.⁴⁴⁻⁴⁶ Degraded interphasial species such as C_2HO^- , Na^- , Cl^- are more significant in the bare m- $\text{WO}_{2.72}$ films, confirming the effective role of protective Al_2O_3 layer. These degraded electrolytes on NC surface are expected to prohibit efficient ion transport through the layer.

Al_2O_3 ALD also effectively prevented photochromic effect which is important to practical employment of smart windows (Figure C.8 in Appendix C). Without Al_2O_3 ALD, films are colored after UV irradiation because of transfer of protons and electrons into m- $\text{WO}_{2.72}$ generated from decomposed electrolytes due to photogenerated hole transfer. However, Al_2O_3 coated films showed slight optical density change upon UV irradiation confirming efficient blocking of hole transfer to the electrolytes originated from large band gap of Al_2O_3 .

This ALD passivation strategy enabled to study spectroelectrochemical properties of different cation charging behavior on m- $\text{WO}_{2.72}$ nanorods film. As can be seen in the m- $\text{WO}_{2.72}$ structure (Figure 4.1 d), there are three types of tunnel sites, hexagonal tunnel, square window, and trigonal cavity similar to the hexagonal tungsten oxide. For the trigonal

cavity, the center to oxygen distance is 155 pm where the Na^+ (radius = 102 pm) is hard to fit while Li^+ (radius = 76 pm) can occupy. It has been also reported that trigonal cavity site is the most stable site for Li^+ ion occupation and expected that Li^+ ions occupy first in the trigonal cavities.³²⁻³⁴ For the lithium ions, the site occupation happens in the order of trigonal cavity, hexagonal tunnel, and square windows. For the sodium ions, there is possibility of ion occupation from either hexagonal tunnel (533 pm) or square windows (346 pm). However, earlier work studied Na^+ are more likely to occupy in the tunnel sites such as hexagonal or pentagonal sites which is larger than square windows.⁴⁷⁻⁴⁹ So, we anticipated Na^+ occupy hexagonal sites and the difference occupation of Li^+ and Na^+ will affect spectroelectrochemical property difference.

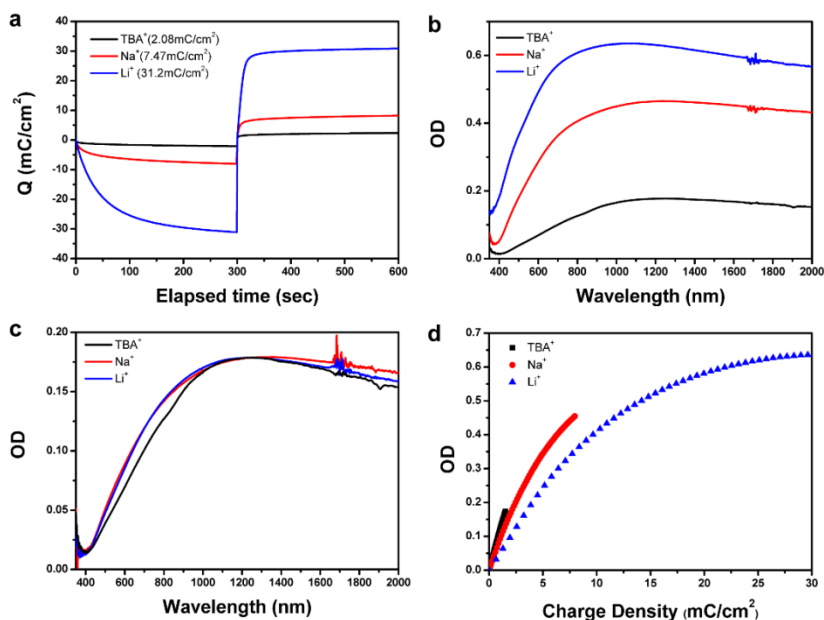


Figure 4.3 Spectroelectrochemical property of 1 nm Al₂O₃ coated m-WO_{2.72} films with different electrolytes. (a) Chronoamperometric charging and discharging curve from Na⁺, Li⁺, and TBA⁺ electrolytes with similar charging potential from OCP. (b) Optical density change at the charge density from (a). (c) Optical spectra difference with same peak intensity at 1200nm with different state of charge. (d) Charge density and optical density change from chronopotentiometric charging.

First, we applied similar potential from its OCP to the different electrolytes system. TBA⁺ electrolytes system gives double-layer capacitive charging behavior as noted from the cyclic voltammetry data (Figure C.9 in Appendix C), and limited capacity and modulation. For the Na⁺ ions, it gives enhanced modulation and increased capacity than TBA⁺ electrolytes system, confirming the ion insertion into the NC structure. However, the capacity and optical modulation is limited than Li⁺ ion system. Larger size of Na⁺ gives large potential barrier to trigonal and square window sites occupation compared to Li⁺.

However, interestingly, the optical modulation per unit charge was greater for sodium ion system than lithium ion system as shown in Figure 4.3 d. This can be explained by occupation of sodium ion in specific site more efficient than lithium ion occupation site. As mentioned earlier, lithium starts to occupy the trigonal cavity, followed by hexagonal tunnel while sodium ions are expected to occupy mainly hexagonal tunnel sites, which means trigonal cavity is not the best site for enhanced coloration. Balaji *et al.* demonstrated coloration process is mainly from lithium ion occupation of hexagonal windows and square

windows sites, not trigonal cavity.³² Corroborating these arguments, our results also show trigonal cavity site is not the best for enhanced coloration.

Understanding of optical modulation behavior is important and this can be elucidated studying from different size of ions. Dahlman *et al.* observed different optical modulation effect by comparing non-intercalating TBA^+ and intercalating Li^+ electrolytes system and figured out independent optical modulation in the visible and near-infrared range from polaronic and LSPR absorption.¹ By comparing spectra of Na^+ , Li^+ , and TBA^+ electrolytes with similar optical density at 1100 nm while different state of charging, we could observe intercalation effect on the optical property changes. For the TBA^+ of non-intercalating ions, absorbance was notable in the near-infrared. But Na^+ and Li^+ show more optical contribution from visible region which might come from the polaronic absorption contribution from intercalation with near-infrared modulation coming from LSPR modulation, which is different with independent modulation of near-infrared and visible light in case of Nb-doped TiO_2 films.

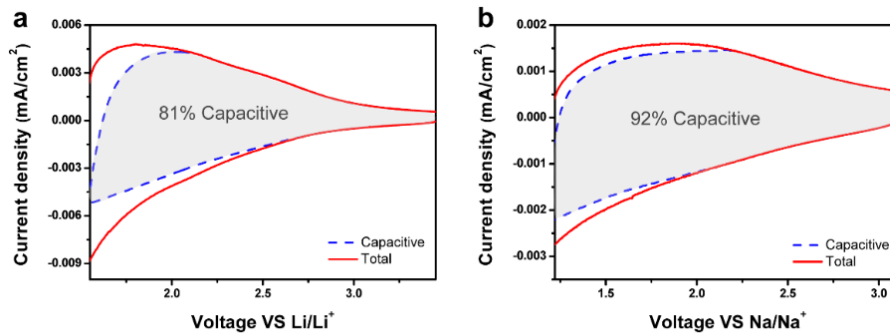


Figure 4.4 Voltammetric response (1 mV/s) for 1 nm Al₂O₃ layer deposited m-WO_{2.72} films with (a) Li⁺ electrolytes and (b) Na⁺ electrolytes. Capacitive contribution to charge storage is shaded.

Different site occupation of different ion affects not only optical modulation but also electrochemical properties. Charge storage kinetics can be derived from cyclic voltammetry (CV) analysis of different scan rate. It assumes current at certain potential consists of capacitive and diffusion-controlled contribution as following equation. $i(V) = k_1 v$ (capacitive) + $k_2 v^{1/2}$ (diffusion-controlled) So capacitive portion can be calculated from k_1 value derived by fitting of different scan rate. Notably, Na⁺ ion system's capacitive portion is high. Reason for giving higher capacitive contribution is from both factors of highly porous thin films giving high surface-to-volume ratio as well as intracrystalline large size of hexagonal tunnels. Interestingly, compared to previous report of aqueous Na⁺ system in hexagonal tungsten oxide where Na⁺ cannot transverse the hexagonal tunnels, Na⁺ diffuse into the structure in our case. It is possibly from solvating molecules of propylene carbonate are desolvated. From the bare CV, we could see the rectangular shape of curve indicating the double-layer capacitive behavior with sloping meaning Na⁺ insertion happens from hexagonal tunnels while there is transport resistance of Na⁺ through the pores (Figure C.10 in Appendix C). For the Li⁺, the capacitive charging portion is 81%. This can be explained from following reason. Li⁺ access more site of tunnels which gives more charging capacity while limited sites give increased diffusion-controlled portion.

4.4 CONCLUSION

In summary, from the non-intercalating bulky ion and different size of ions that can intercalate into the structure while exhibiting different site occupation, we studied cation size effect on spectroelectrochemical properties. Model system of porous m-WO_{2.72} films were fabricated from solution deposition of ligand-stripped nanorods from electrostatic repulsion. Al₂O₃ ALD plays an important role in preventing severe degradation while allowing Na⁺ and Li⁺ diffusion into the structure. Different size of ions gave different degree of intercalation, inducing different spectroelectrochemical modulation. We also demonstrated that Na⁺ switching can be increased by nanostructuring as well as considering its diffusion sites. Our result shows the importance of understanding of the ion's site occupation in crystal structure and their spectroelectrochemical properties. This will suggest the better way of designing the NC thin film system for different electrolytes.

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Chapter 5: Conclusion and Future Work

5.1 CONCLUSION

Even same material of same phase shows significant different spectroelectrochemical properties when the size narrow downs to nanoscale regime. If the crystal size is nanoscale and carrier density is high enough to give free electrons above conduction band, LSPR absorption emerges. Moreover, charging behavior also changed from dominant diffusion-controlled behavior to mostly capacitive charging behavior. Arrangement of different shape nanocrystals is also important to change these properties. All these properties can positively make impacts on electrochromic performance. As confirmed from chapter 2, arrangement of anisotropic nanorods can not only open the porosity but also new functionality from incorporating guest molecules. From chapter 3, by understanding mechanistic optical modulation behavior of precisely tuned nanocrystals, we could design the targeted ‘on and off’ reflected electrochromic Bragg stacks. This research emphasize how precisely tuned nanocrystals can be effectively utilized for optimizing the targeted performance of Bragg stacks. Chapter 4 studied how different size of tunnels affects spectroelectrochemical properties of electrolytes with different cation size and efficiently used for improving the performance of Na^+ -based electrolytes system. We confirmed that performance based on Na^+ electrolytes system can be improved by understanding spectroelectrochemical properties relation with its site occupation.

5.2 FUTURE WORK

Control alignment of nanorods from spray-coating method

Efficient utilizing the anisotropic properties of nanocrystals can improve the electrochromic performance. In chapter 2, the random porous film from nanorods were fabricated by the spin-coating process which induces more horizontal alignment of nanorods from shear force of spin-coating process. Different method of spray coating can possibly generate more porous structure from vertical alignment of nanorods from vertical direction of solvent evaporation.

Shape and crystalline anisotropic effect on spectroelectrochemical properties

Both shape and crystalline anisotropic properties of nanocrystals can contribute to analyzing the spectroelectrochemical properties. In a previous study, different shape of Cs:WO₃ nanocrystals were established (Figure 5.1 and 5.2).¹ Hexagonal tungsten oxide nanocrystals have crystalline and shape anisotropic properties, so their LSPR properties are influenced by both factors. However, spectroelectrochemical properties of hexagonal tungsten oxide nanocrystals have not been studied even though this can give rich information of spectroelectrochemical evolution by comparing different shape of nanocrystals.

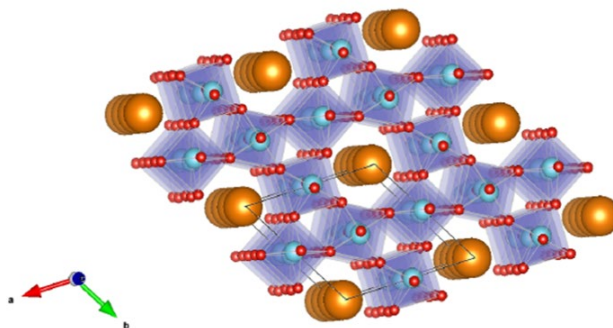


Figure 5.1 Crystal structure of hexagonal Cs-doped tungsten oxide.

If Cs-doped tungsten oxide nanocrystal thin films have similar volume and surface area while different shape, it will show very different spectroelectrochemical behavior depending on the size of electrolytes ions. For example, non-intercalating bulky ions such as tetrabutylammonium ion (TBA^+) cannot intercalate into the nanocrystal structure, so they will show similar electrochemical properties. However, if sodium and lithium ions are used as electrolytes, different spectroelectrochemical properties are expected.

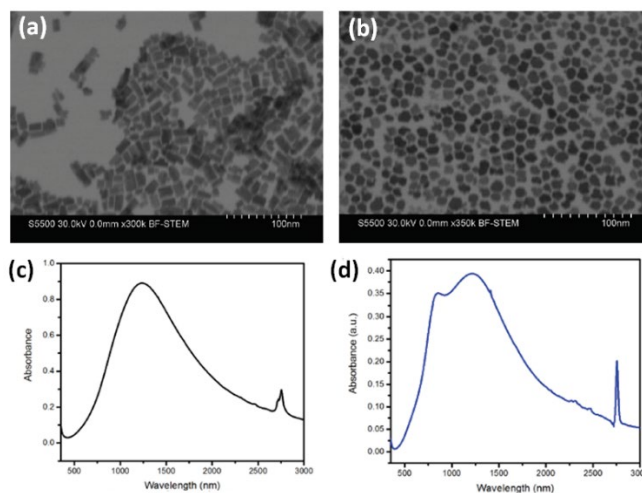


Figure 5.2 STEM image (a) and absorbance (c) of Cs:WO₃ nanorods and STEM image (b) and absorbance (d) of Cs:WO₃ platelets

First, for the electrochemical properties, TBA⁺ electrolytes system is expected to show capacitive behavior and similar degree of capacity if the volume and surface area is similar. If the intercalation happens into the crystal with different cation electrolytes such as sodium or lithium ions, interstitially doped Cs needs to be taken account. For the Na⁺ electrolytes system, platelet shape can give more capacity than nanorods, because accessible area is larger than that of nanorods assuming that Cs diffusion is slow or stationary. As can be seen in Figure 5.3, sodium ions cannot access to the interstitial space between Cs ions. So, the platelets are expected to show more capacity than nanorods case. For the Li⁺ electrolytes system, it might access to space between Cs ions because Li⁺ ions are small enough to occupy in the trigonal cavity, so it can insert into the space between Cs ions through trigonal cavity.

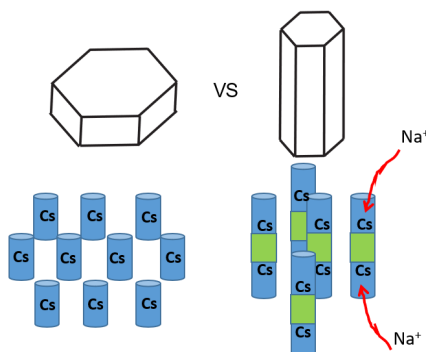


Figure 5.3 Possible interstitial Cs effect on Na⁺ diffusion in different shape of nanocrystals

For the optical properties, TBA⁺-based electrolytes are expected to give capacitive charging and limited modulation from limited capacity. Na⁺ systems are expected to show higher coloration efficiency than Li⁺ system because trigonal cavity is not a best coloration

tunnel site. Using Na^+ as electrolytes system, nanoplatelet might give more optical modulation than nanorods at the same applying potential given the hypothesis of limited accessible space of nanorods. However, Li^+ might give similar optical modulation from both nanorods and nanoplatelet. In order to prove this, precise controlling of the nanocrystals with different morphology is required as well as proper film processing is needed to make uniform film in order to compare different system.

5.3 REFERENCE

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Appendices

Appendix A: Template-free Mesoporous Electrochromic Thin Films on Flexible Substrates from Anisotropic Tungsten Oxide Nanocrystals

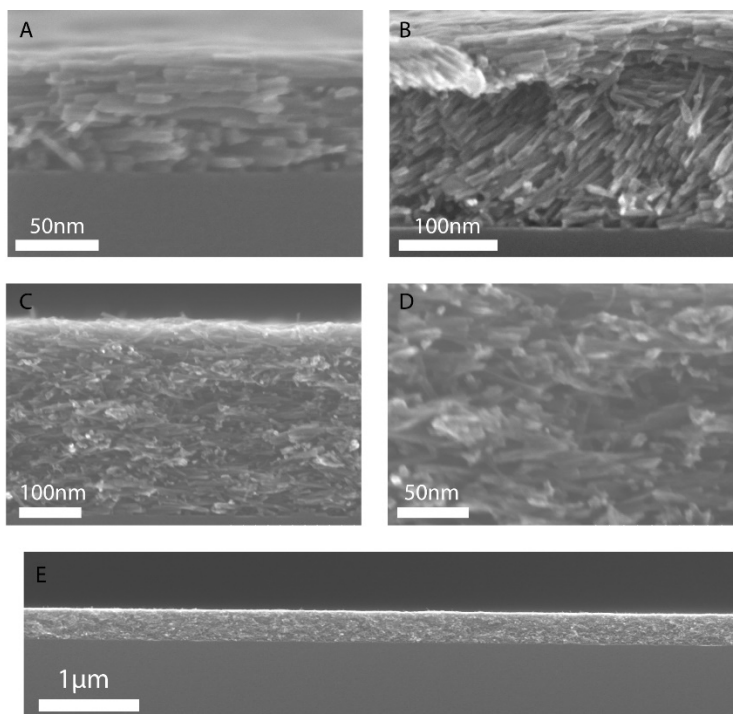


Figure A.1 SEM cross-section images of packed films in different regions (A,B) and random film with different magnifications (C,D,E) using high aspect ratio nanorods.

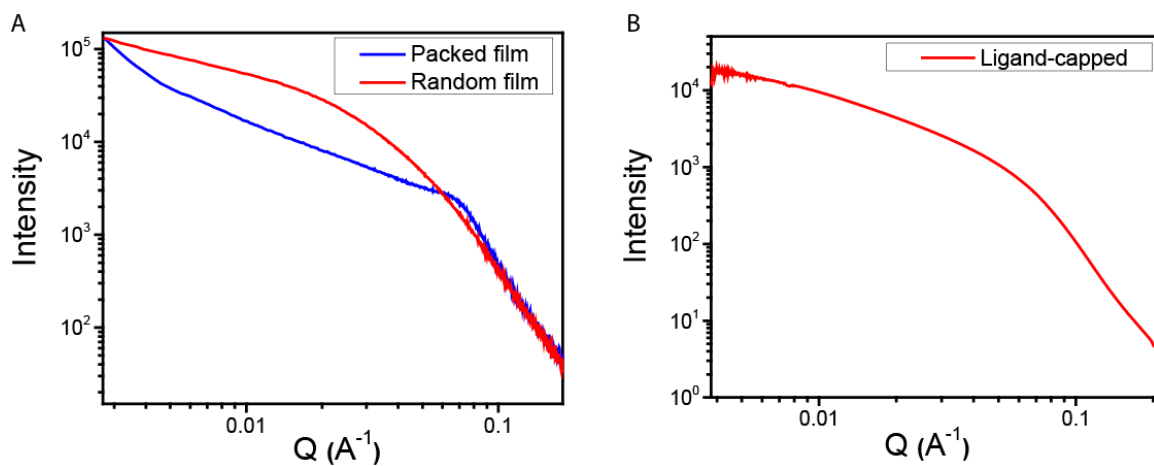


Figure A.2 GISAXS data of packed and random nanorod films on silicon substrates (A) and SAXS data for ligand-capped nanorods in toluene (60 mg/mL) (B) using high aspect ratio nanorods.

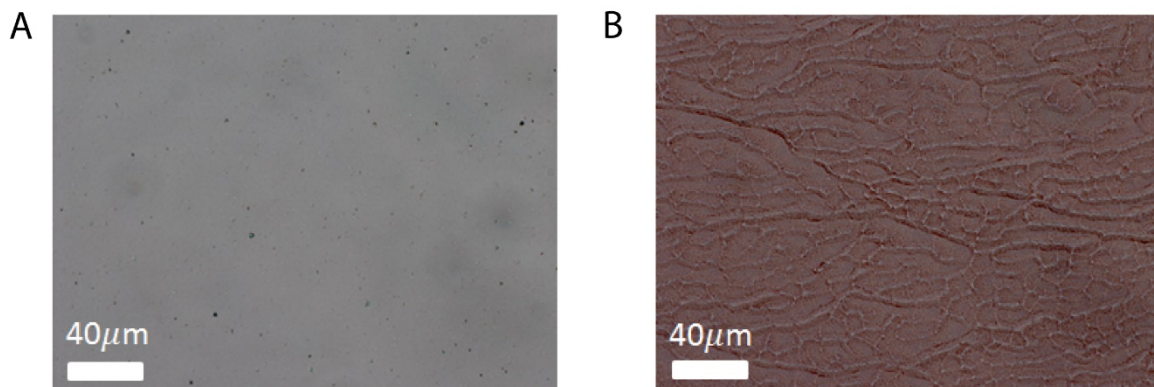


Figure A.3 Optical microscope images of ligand-stripped (A) and ligand-capped films (B) using high aspect ratio nanorods. The images were taken at 20 $\times$ magnification.

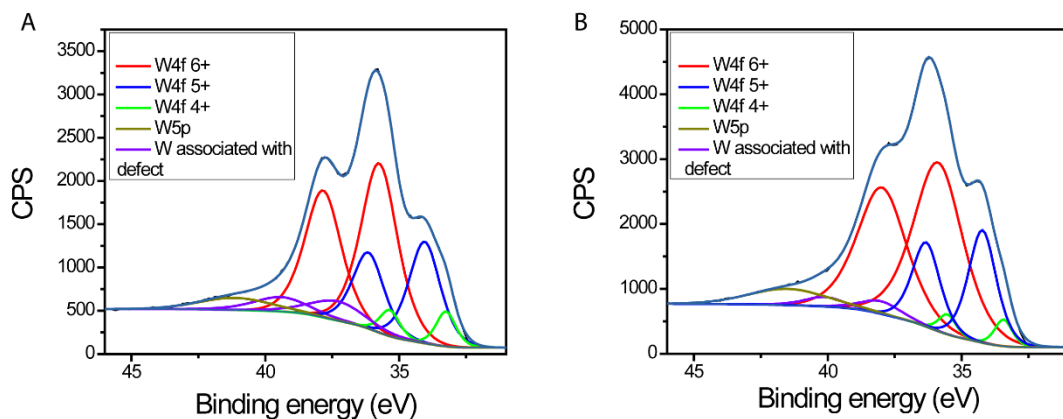


Figure A.4 Air-free XPS analysis of $\text{WO}_{2.72}$ nanorods films on HOPG (A) before ligand-stripping and (B) after ligand-stripping. O:W ratio is increased from 2.18 to 2.49 after ligand-stripping.

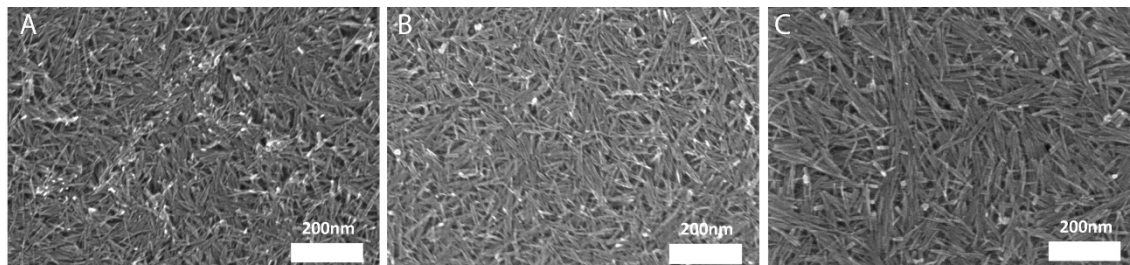


Figure A.5 Top-down SEM images of spin coated films made at 200rpm (A), 700rpm (B) and drop cast films prepared in a glovebox (C).

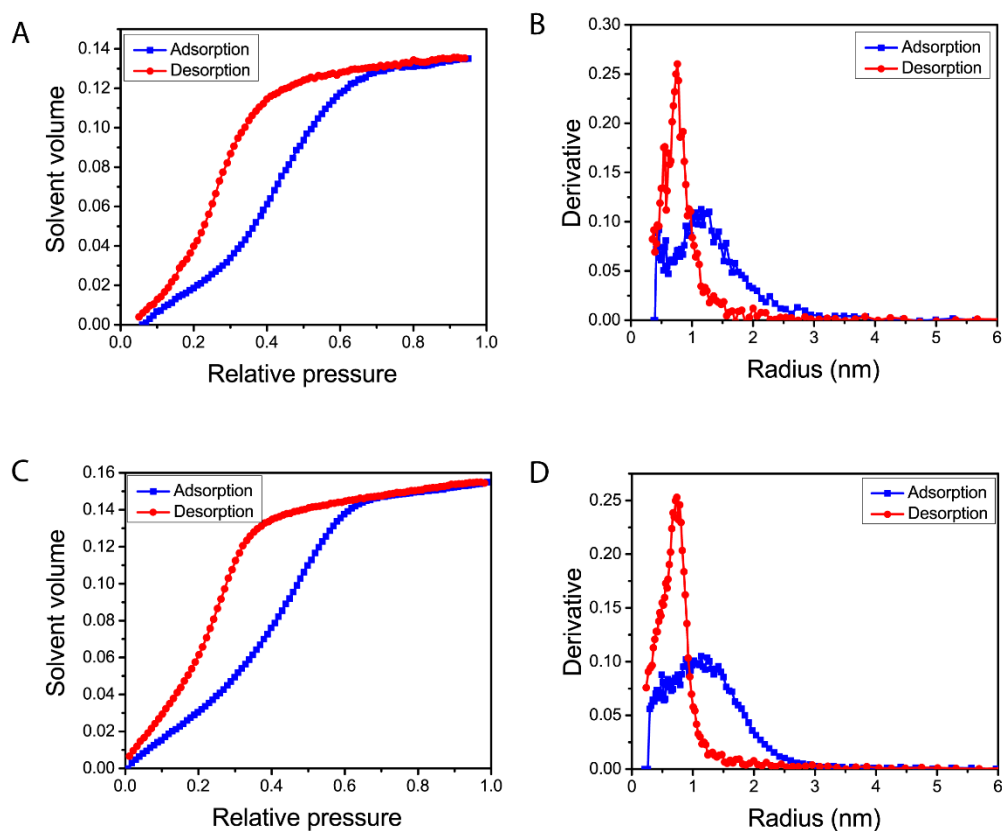


Figure A.6 Porosity and pore size distribution measured by ellipsometric porosimetry. (A,C) Porosity of high (A) and low (C) aspect ratio nanorods in packed films (C). (B,D) Pore size distribution of high (B) and low (D) aspect ratio nanorods in packed films. Ligand-capped nanorod films for ellipsometric porosimetry measurement were annealed to remove the porogens.

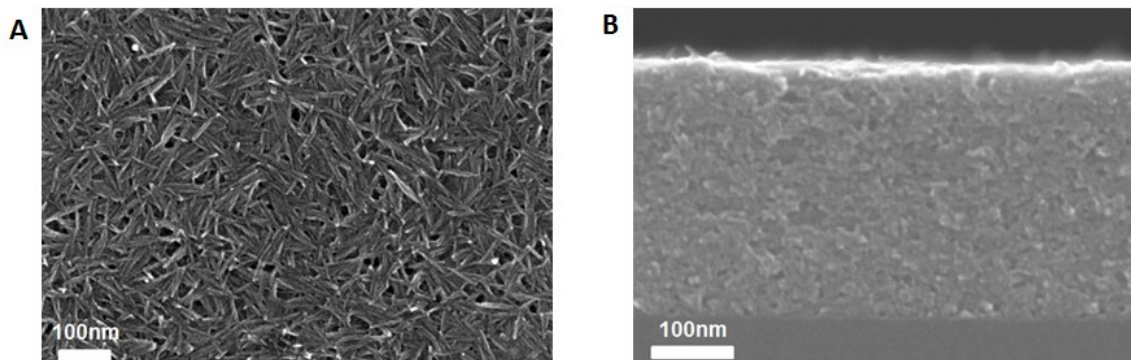


Figure A.7 SEM images of $\text{WO}_x\text{-NbO}_x$ composite films using high aspect ratio nanorods with (A) top-view and (B) cross-section view.

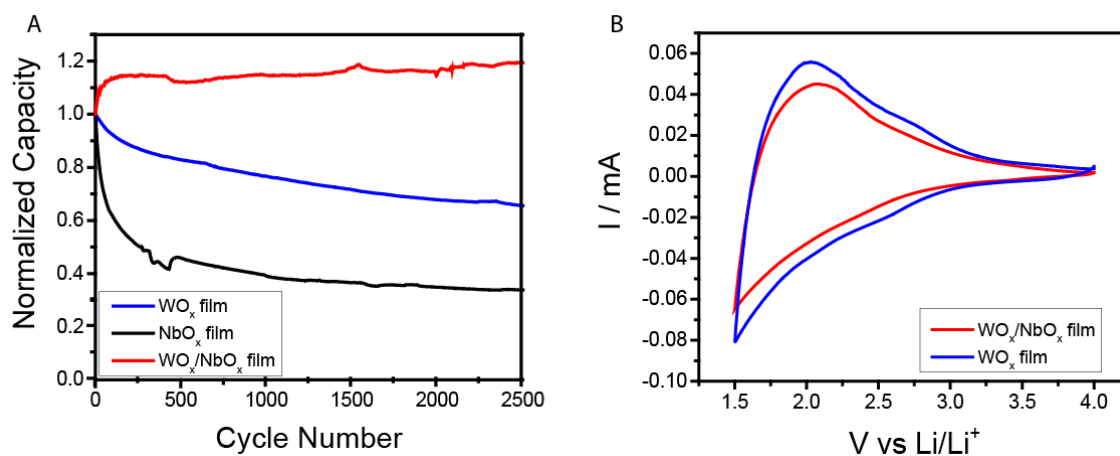


Figure A.8 (A) Normalized charge capacity of $\text{WO}_{2.72}$ only film, NbO_x only film, and $\text{WO}_x\text{-NbO}_x$ composite film. Samples were cycled by cyclic voltammetry method between 1.5-4V. (B) Cyclic voltammetry of $\text{WO}_{2.72}$ only film and $\text{WO}_x\text{-NbO}_x$ composite film with 1mV/sec scan rate.

Appendix B: On/Off Tunable Electrochromic Bragg Stacks from Doped Semiconductor Nanocrystals

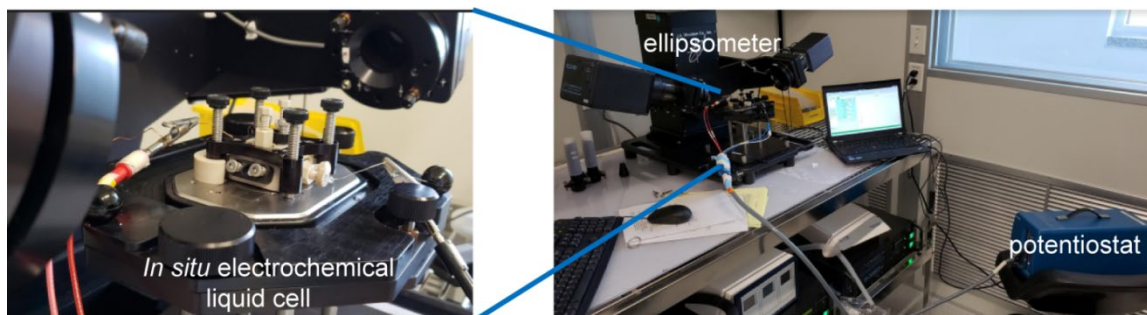


Figure B.1 Optical photographs of *in situ* electrochemical ellipsometry setup.

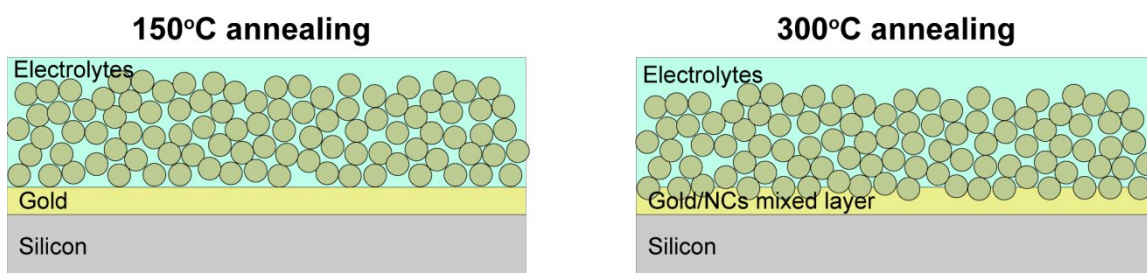


Figure B.2 Model layer stacks used for *in situ* ellipsometry data analysis. Including a mixed gold/NCs layer was necessary to fit the data of samples annealed at 300°C.

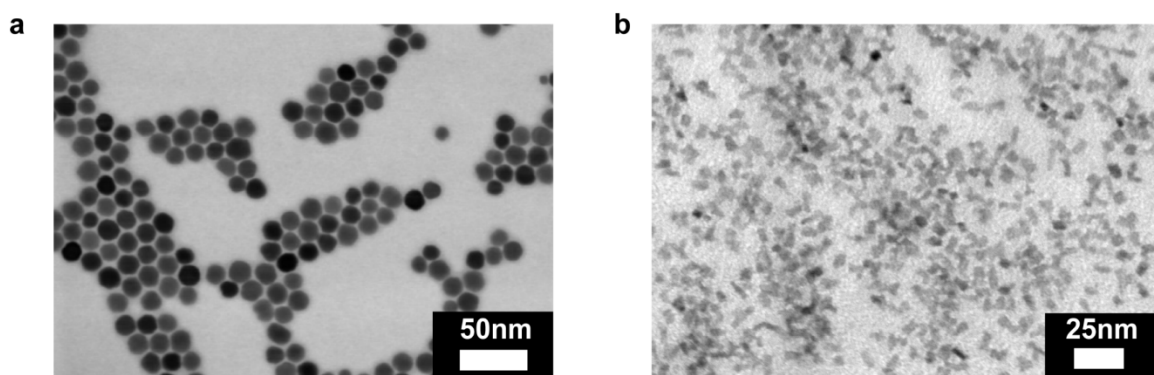


Figure B.3 STEM images of (a) 15 nm sized 0.4 at%-doped ITO NCs and (b) 5 nm sized WO_{3-x} NCs.

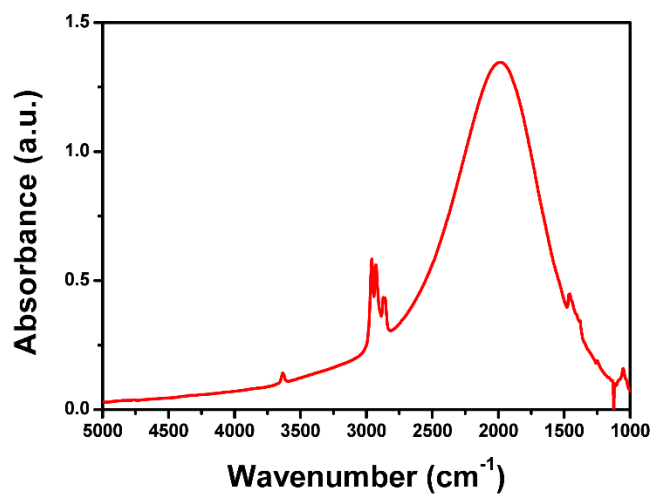


Figure B.4 FTIR spectrum of 15 nm sized 0.4 at%-doped ITO NCs dispersed in tetrachloroethylene.

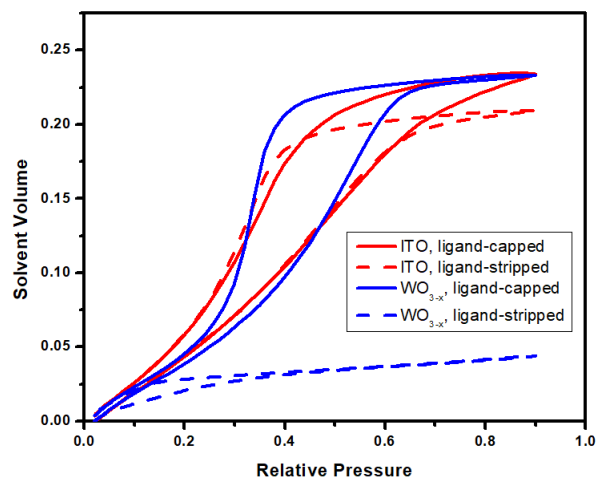


Figure B.5 Porosity measured by EP. Porosity of ITO and WO_{3-x} NC thin films prepared from ligand-capped and ligand-stripped NCs. NC thin films deposited from ligand-capped NCs were annealed at 400 °C to remove the organic ligands on the NC surface before EP measurement.

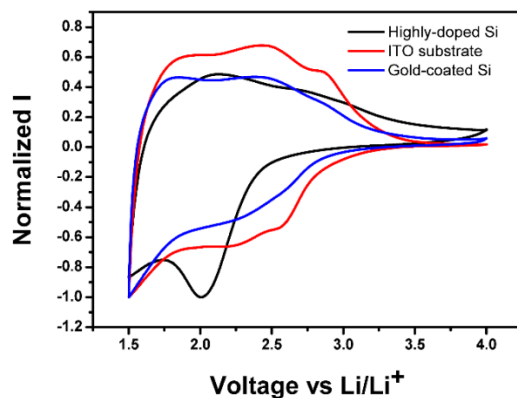


Figure B.6 Substrates effect on the cyclic voltammetry response of 300°C-annealed WO_{3-x} NC film with a 1 mV/s scan rate.

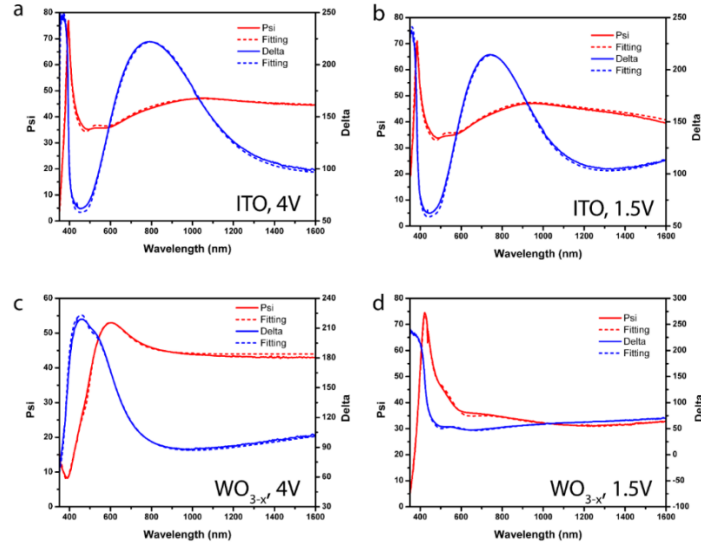


Figure B.7 Original psi and delta data and their fitting for ITO NC thin films discharged at 4 V (a) and charged at 1.5 V (b), and WO_{3-x} NCs thin films discharged at 4 V (a) and charged at 1.5 V (d). A final annealing process at 300°C was employed for these samples.

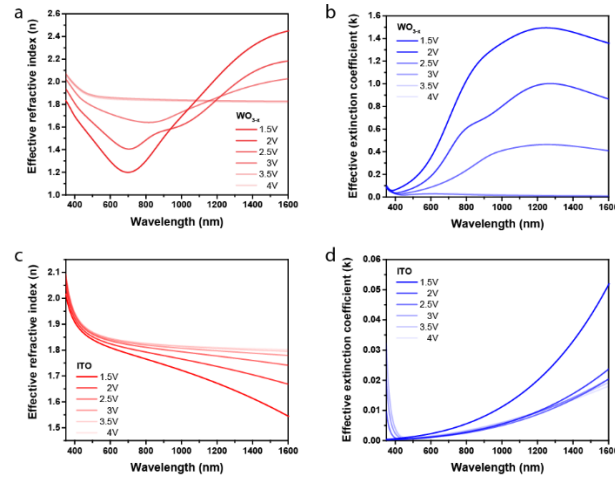


Figure B.8 Effective refractive index (n) and extinction coefficient (k) of ITO (a,b) and WO_{3-x} NC (c,d) thin films in electrolyte at different potentials from 4 to 1.5 V with 500 mV step size. These results are derived by fitting the data represented in Figure S7.

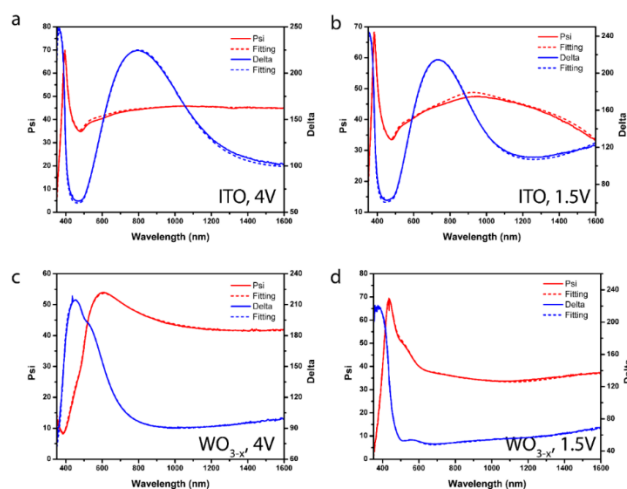


Figure B.9 Original psi and delta data and their fitting for ITO NC thin films discharged at 4 V (a) and charged at 1.5 V (b), and WO_{3-x} NC thin films discharged at 4 V (a) and charged at 1.5 V (d). A final mild annealing process at 150°C was employed for these samples.

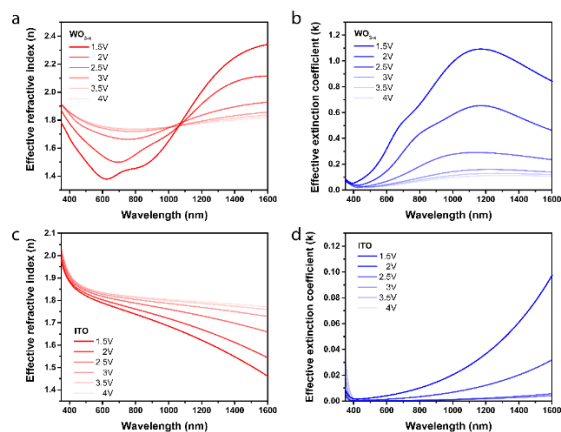


Figure B.10 Effective refractive index (n) and extinction coefficient (k) of ITO (a,b) and WO_{3-x} NC (c,d) thin films in electrolyte at different potentials from 4 to 1.5 V with 500 mV step size. These results are derived by fitting the data represented in Figure S9.

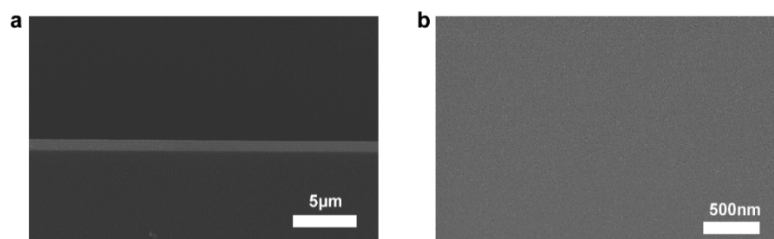


Figure B.11 SEM cross-sectional (a) and top-view (b) images of ITO NC 165 nm/ WO_{3-x} NC 55 nm Bragg stack with 4 bilayers (BS1).

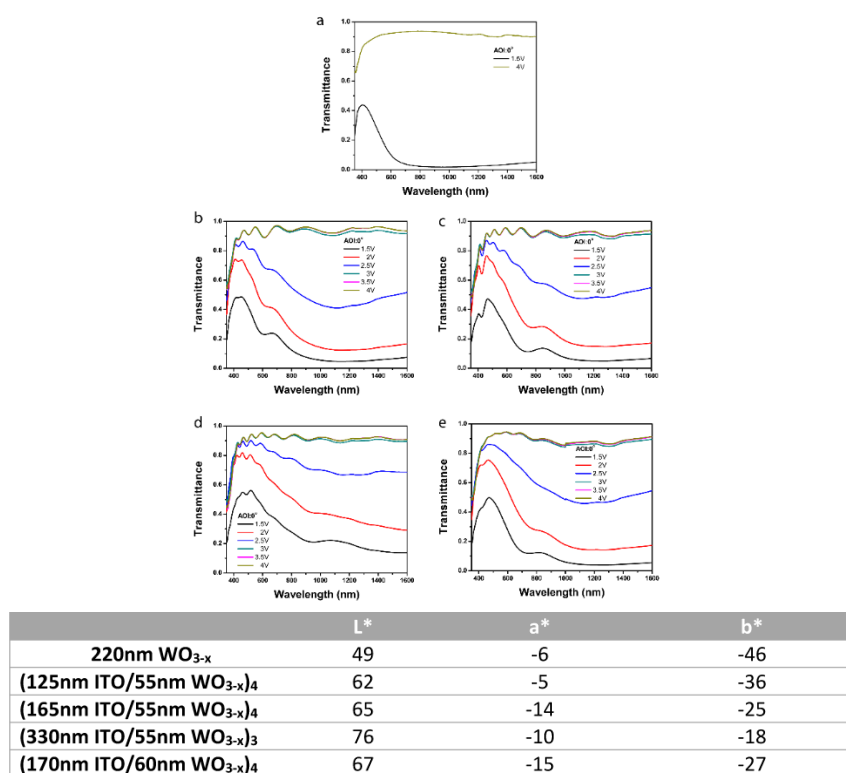


Figure B.12 Transmittance data with near 0 degree AOI of (a) a 220 nm-thick WO_{3-x} NC film, (b) a 125 nm ITO/ 55 nm WO_{3-x} Bragg stack with 4 bilayers (BS2), (c) a 165 nm ITO/ 55 nm WO_{3-x} Bragg stack with 4 bilayers (BS1), (d) a 330 nm ITO/ 55 nm WO_{3-x} Bragg stack with 3 bilayers (BS3), and (e) a 170 nm ITO/ 60 nm WO_{3-x} Bragg stack with 4 bilayers (BS4). Samples represented in a-d were annealed at 300°C and e was annealed

at 150°C. The table shows the CIELab color space coordinates under D50 illuminant for transmitted light at 1.5 V for all five samples.

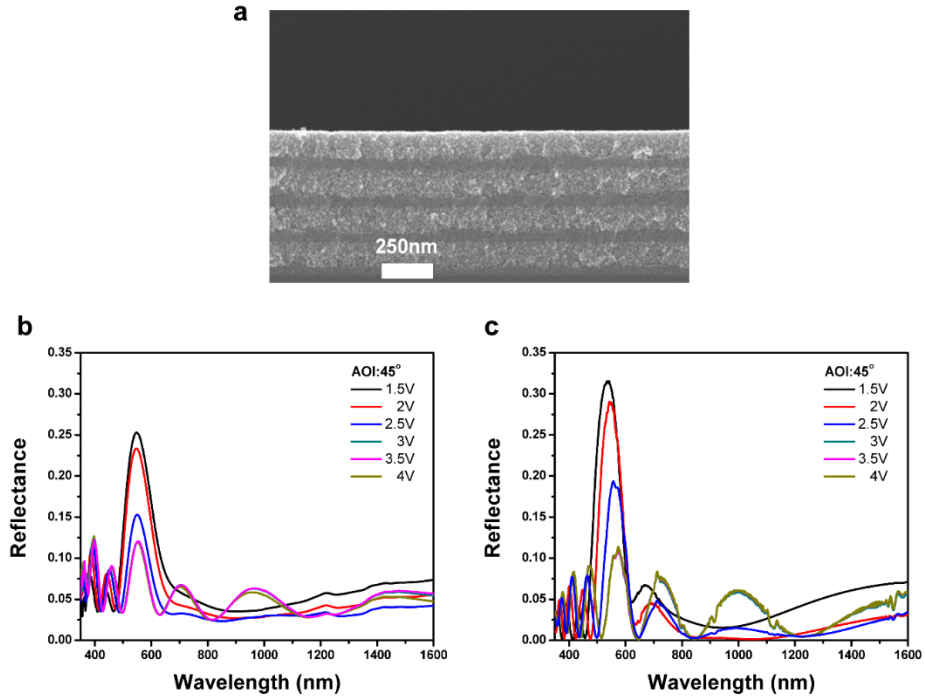


Figure B.13 (a) SEM cross-section image of 125 nm ITO/ 55 nm WO_{3-x} with 4 bilayers (BS2), (b) experimental and (c) simulated reflectance data.

Appendix C: Cation-dependent Spectroelectrochemical Properties of Plasmonic Tungsten Oxide Nanocrystal Thin Films with Al₂O₃ Passivation

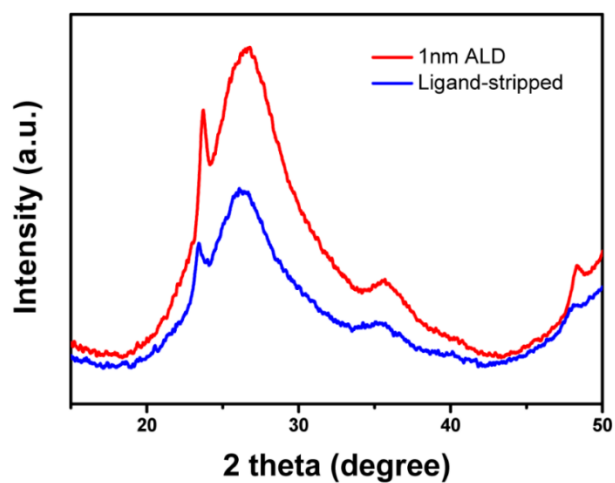


Figure C.1 XRD patterns of bare ligand-stripped and 1nm Al₂O₃ deposited m-WO_{2.72} films. Both films are fabricated by spin-coating process.

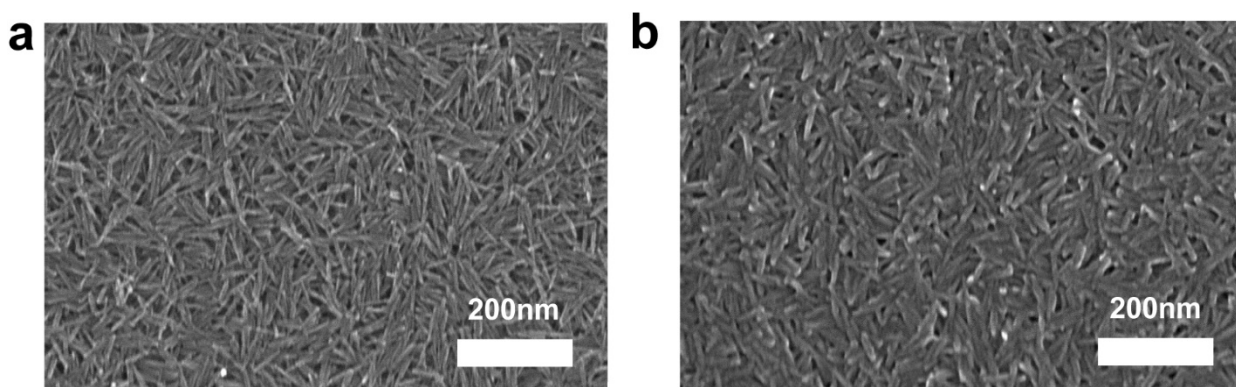


Figure C.2 SEM image of (a) bare and (b) 2nm Al_2O_3 deposited m- $\text{WO}_{2.72}$ films

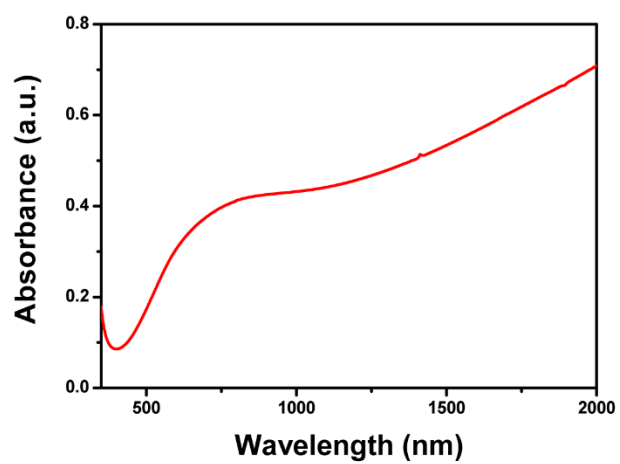


Figure C.3 Absorbance spectra of m- $\text{WO}_{2.72}$ nanorods dispersed in tetrachloroethylene

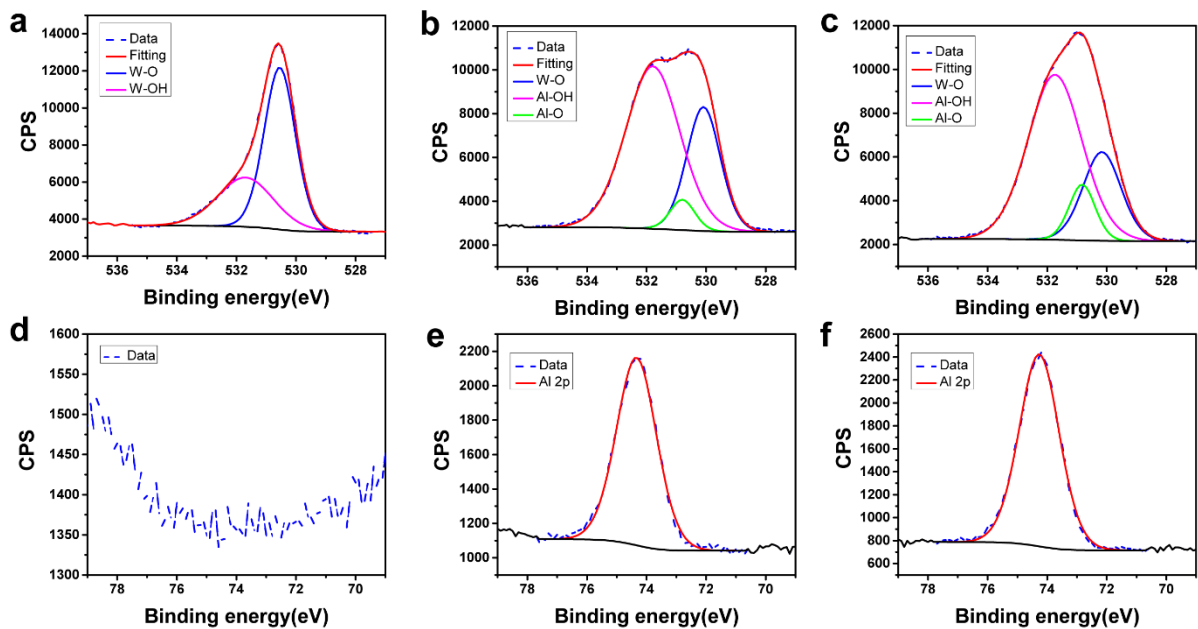


Figure C.4 XPS analysis of bare (a,b), 1 nm Al_2O_3 ALD (b,e), and 2 nm Al_2O_3 ALD (c,f) films. a,b, and c are O 1s peak and e,f are Al 2p peaks.

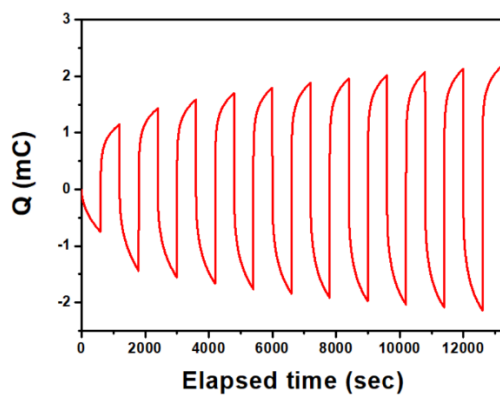


Figure C.5 Chronoamperometry cycling between 3.67 V and 1.17 V of 2 nm Al_2O_3 coated $\text{m-WO}_{2.72}$ films.

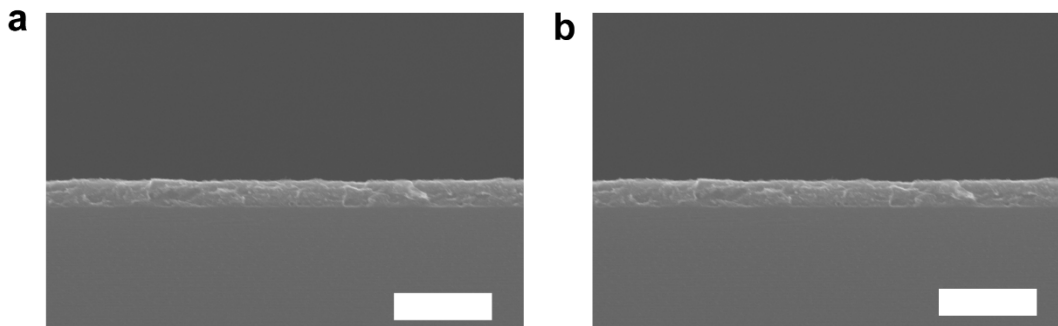


Figure C.6 (a) bare films and (b) 1nm ALD films after 400 cycling

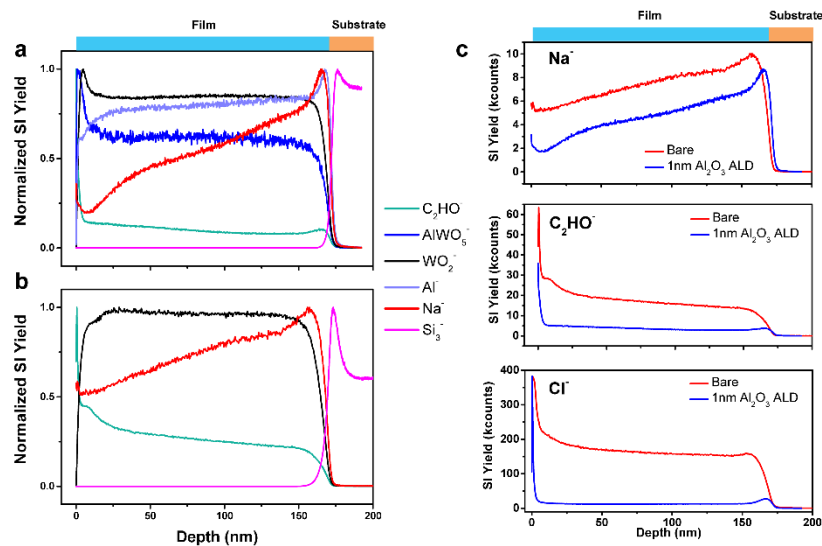


Figure C.7 Normalized depth profiling of several secondary ion fragments of interest at the 30 cycled 1 nm Al_2O_3 deposited (a) and bare (b) m- $WO_{2.72}$ films. (c) Depth profiles of secondary ion fragments of interest (Na^+ , Cl^- , and C_2HO^-) at 30 cycled 1nm Al_2O_3 deposited and bare m- $WO_{2.72}$ films.

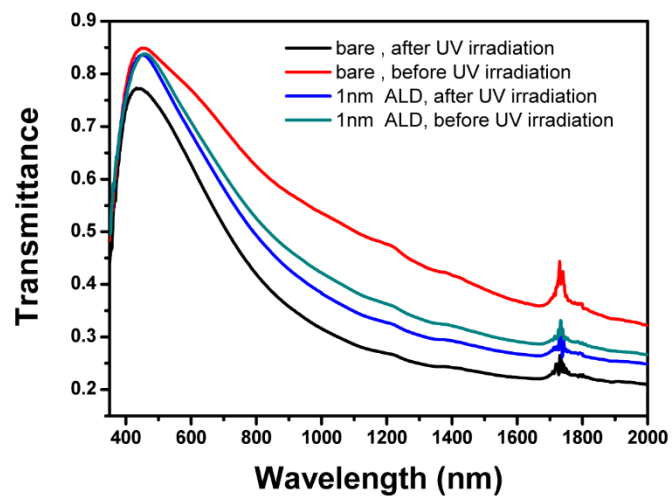


Figure C.8 Transmittance data after UV irradiation experiments

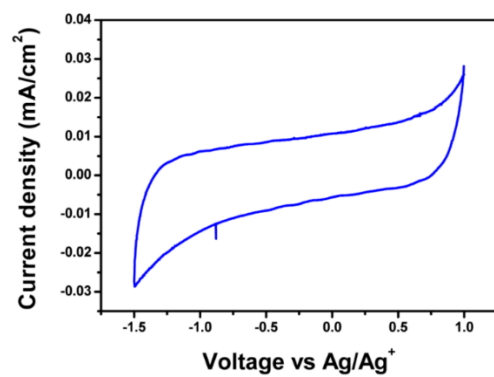


Figure C.9 CV of 1 nm Al_2O_3 deposited on $\text{m-WO}_{2.72}$ from ALD

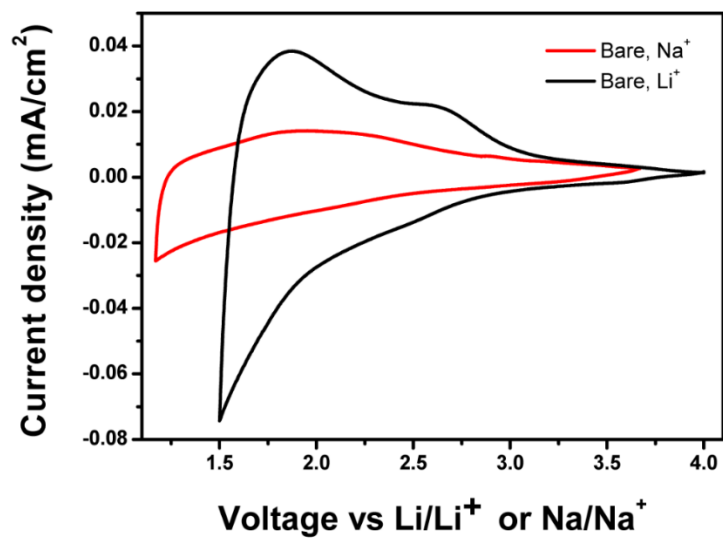


Figure C.10 CV with 2 mV/s scan rate for bare films with Na⁺ and Li⁺ electrolytes system

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