

基于氧化钨和氧化镍的电致变色器件研究进展

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摘要: 电致变色器件(Electrochromic Devices, ECDs)是一种颜色变化受电压调控的智能装置, 具有工作温度范围宽、光学对比度高、可逆双稳态性能好、驱动电压低和能耗低等优点, 在智能动态调光窗、全彩色电子显示屏、防眩光护目镜、自适应双隐身伪装以及可视化储能等领域展现出了巨大的应用潜力。阴极着色材料氧化钨(WO₃)和阳极着色材料氧化镍(NiO)是两种被广泛研究的无机电致变色材料, 由WO₃和NiO薄膜组成的互补型电致变色器件在大规模智能窗的应用中具有极高的商业价值。改善电致变色器件的综合性能如光学调制范围、响应速度、循环寿命和耐候性等问题一直备受关注。本文围绕互补型电致变色器件的结构组成, 综述了基于WO₃和NiO的电致变色全器件的近期研究进展。首先分别阐述了WO₃和NiO薄膜的电致变色机理和衰退机制, 讨论了改进制备工艺、元素掺杂改性、设计纳米结构和引入复合材料这四种薄膜性能优化策略的作用和最新研究进展, 其次, 按照器件的组成成分和结构设计介绍了互补型电致变色全器件的分类体系, 总结了各组分材料的选择和器件结构对器件综合性能的影响, 最后对电致变色器件的应用前景和发展趋势进行了展望。

关键词: 电致变色器件; 氧化钨; 氧化镍; 综述

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Electrochromic Devices Based on Tungsten Oxide and Nickel Oxide: a Review

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Abstract: Electrochromic devices (ECDs) are the intelligent devices change color by applying electric potential, with the advantages of wide working temperature, high optical contrast, good reversible bistability, low driving voltage, and low energy consumption, which show great application potential in the field of dynamic smart windows, full-color electronic screens, anti-glare goggles, adaptive dual-stealth camouflage, and energy storage status visualization. Cathodically coloring material tungsten oxide and anodically coloring material nickel oxide are two widely studied inorganic electrochromic materials, and complementary electrochromic devices based on WO₃ and NiO films have high commercial values in the application of large scale smart windows. Improving the performance of the complementary ECDs such as optical modulation range, response rate, cycle life and weather fastness has attracted much attention. This review focuses on the structural composition of complementary electrochromic devices and

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summarizes the recent research progress of the electrochromic full devices based on WO_3 and NiO . Firstly, the electrochromic mechanism and decay mechanism of WO_3 and NiO films are clarified, the effects and latest research progress of four strategies for film performance optimization that include optimizing preparation conditions, element doping modification, designing nanostructure, and introducing composite materials are discussed in detail. Secondly, according to the composition and structure design of the device, the classification system of the complementary electrochromic full device is introduced, and the influence of selection for each component material and the device structure on device overall performance are summarized. Finally, the application of the electrochromic device prospects and development trends are forecasted.

Key words: electrochromic device; tungsten oxide; nickel oxide; review

电致变色(Electrochromic, EC)是指材料的光学特性如透过率、反射率、发射率等在外电场的控制下发生稳定、可逆变化的一种智能调控技术, 断压后的电致变色器件仍能在着色和褪色两种状态之间保持稳定, 这种仅需在变色的一瞬间施加电压的低能耗性使其在节能建筑中具有独一无二的优势, 尤其是在办公大楼的智能窗和客机舷窗等领域应用广泛。

自1969年Deb研制出第一个基于 WO_3 的电致变色器件以来^[1], 提高电致变色器件性能的研究一直是人们关注的重点。目前大多数的电致变色器件仍存在颜色或透过率调制范围小、响应速度慢、循环稳定性差、装配工艺不完善和难以大规模制备等种种问题, 而发挥阴极和阳极电致变色材料协同补色作用的互补型器件在提高光学对比度和循环寿命等方面的作用已得到普遍认可, 并大规模运用在智能窗的商业化生产中。阴极电致变色材料是指在发生还原反应时着色的一种无机过渡金属氧化物^[2-3], 包括 WO_3 、 TiO_2 、 Ta_2O_5 等^[4], 其中 WO_3 作为最早被深入研究的电致变色材料, 其变色机理相对清晰, 制备工艺也日趋成熟, 常用作互补型电致变色器件中的关键变色层。有多种适合与 WO_3 组成互补型器件的阳极电致变色材料, 如 IrO_2 ^[5]、 V_2O_5 ^[6]和 NiO ^[7]等, 其中 NiO 是最具前途的一种阳极电致变色材料, 具有光学调制范围大、着色效率高和循环耐久性好等诸多优点, 在互补型电致变色器件中常被用作 WO_3 的对电极。

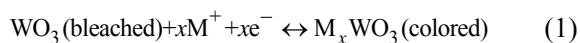
本文综述了基于 WO_3 和 NiO 的电致变色器件的最新研究进展, 介绍了 WO_3 和 NiO 两种典型电致变色薄膜的变色机理、衰退机制和制备工艺, 重点讨论了提高 WO_3 和 NiO 薄膜性能的几种有效策略, 随后介绍了透明导电层和离子传导层的材料分类和传统与新型的器件结构设计, 并总结了各层薄膜性质和器件组装方式对全器件性能的影响, 最后展望了互补型电致变色器件的应用前景和未来研究趋势。

1 WO_3 薄膜研究进展

1.1 WO_3 的结构和变色机理

氧化钨是最早被研究的一种阴极电致变色材料, 可分为结晶态 WO_3 和非晶态 WO_3 。晶体 WO_3 由周期性排列的 WO_6 正八面体组成, 是一种类钙钛矿结构, W原子位于八面体的中心, O原子作为连接点使 WO_3 内部形成可供离子传输的多边形通道。非晶态 WO_3 由于相对无序的结构提供了更大的离子通道和更多的反应位点, 往往表现出优异的EC性能, 但稳定性通常不如晶体 WO_3 。

对 WO_3 电致变色机理的研究可追溯到1973年Deb提出的色心模型^[8], 非晶 WO_3 中的氧空位缺陷带正电荷, 能俘获电子形成F色心, 色心不稳定吸收光子产生激发态, 从而导致 WO_3 着色, 但是色心模型无法解释晶体 WO_3 的变色。1975年, Faughnan提出了价间跃迁模型^[9], 又称为双注入模型, 当离子和电子同时注入到 WO_3 薄膜时, WO_3 发生可逆的氧化还原反应, 如式(1):



其中, M^+ 表示 H^+ 、 Li^+ 、 Na^+ 、 K^+ 等阳离子, 电荷在 W^{6+} 和 W^{5+} 之间转移引起 WO_3 光吸收的变化, 薄膜从透明变成蓝色。Schirmer等^[10]提出的小极化子模型也是基于离子和电子共同注入和抽出的观点, 除此之外还有能级模型、配位场模型等理论, 这些变色理论都有各自的局限性, 但离子和电子共同作用的电致变色机理目前已得到普遍认可。

1.2 WO_3 薄膜的衰退机制

WO_3 电致变色薄膜具有大光学调制范围、高着色效率、良好的可逆性等诸多优点, 相比于有机电致变色材料, WO_3 薄膜还能在多次循环过程中保持稳定、可逆的颜色变化, 以及在恶劣的环境中持续

地工作。然而,在长时间的电荷插入和抽出的过程中,WO₃薄膜和器件的EC性能会大幅度下降,如光调制能力减弱、响应时间变长等,严重影响了电致变色器件的实际使用效果。

目前对WO₃薄膜和器件退化机制的研究很少,通常认为薄膜和器件性能下降是由于宿主结构中捕获离子的积累。北京工业大学严辉课题组^[11]将WO₃膜的降解过程分为漂白态和着色态的衰退。如图1所示,着色过程中插入离子电荷密度的降低是导致着色态退化的主要原因,捕获离子的积累还会造成两电极间开路电位(OCP)的衰减,减弱了驱动离子进入薄膜的电场力。该课题组还研究了插入离子数与WO₃薄膜EC性能和退化情况的关系^[12],大量的离子插入虽然在一定程度上提高了薄膜的光调制能力,但会严重破坏薄膜结构,已被捕获的离子难以被提取出来,最终导致WO₃薄膜的快速衰退。

1.3 WO₃薄膜的性能优化

无机电致变色材料WO₃具有从透明态到深蓝色变化的大透过率调制范围和柔和舒适的颜色转换,在智能窗的生产和应用中具有不可比拟的优势,能够调节窗口的透过照明强度以提供舒适的室内环境、美学设计和提高建筑节能效率。然而,WO₃薄

膜的致密性和较低的扩散系数使其切换时间非常长,在需要快速响应的电子设备等领域表现得不尽人意,提高WO₃的响应速度、着色效率仍是当前研究的重点,改进制备方法、掺杂元素、设计纳米结构和复合材料是改善WO₃薄膜性能的几种常用手段。

1.3.1 制备方法

常用的WO₃薄膜生产方法有水热法^[13]、溶剂热法^[14]、溶胶-凝胶法^[15]、电化学沉积法^[16]、喷墨打印^[17]和磁控溅射法^[18]等。由于WO₃薄膜的制备方法多样,每种方法的可调参数较多,所以在不同工艺下制备的WO₃薄膜质量差异很大。水热法是一种高温高压控制晶体生长的方法,但需要先制备晶种层,电子科技大学贾春阳等^[13]研究了一种简单高效制备WO₃薄膜的一步水热法,使用甘油作为自种剂,无需预先制备晶种层,制备出的WO₃薄膜具有15000次的高循环稳定性和78.1%的大光学调制幅度,着褪色时间较短(5 s/6 s)。河南大学蔡国发等^[16]采用了一种新颖的脉冲电化学沉积法制备高性能的多孔WO₃薄膜,这种方法无需模板和热处理,适用于不同的导电基底,其中在ITO玻璃上制备的WO₃薄膜具有97.7%超大光学调制幅度和118.3 cm²/C高着色效率。磁控溅射法是一种常用的

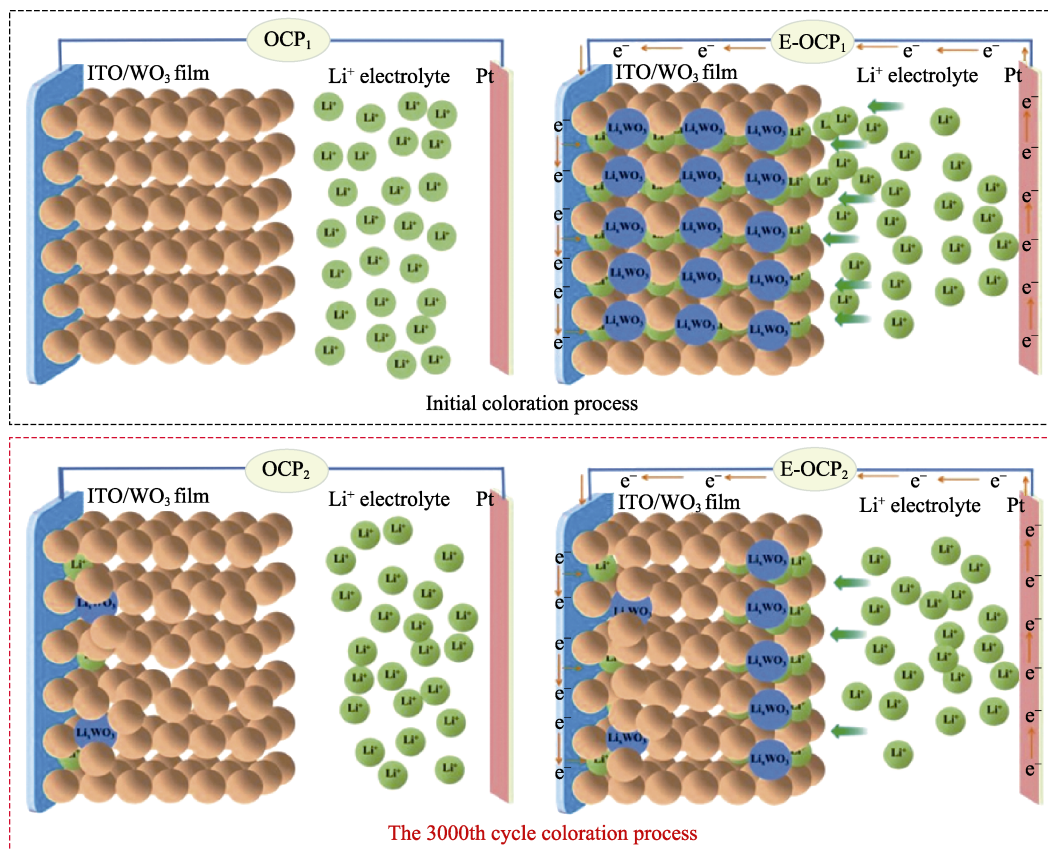


图1 捕获离子对OCP和插入离子电荷密度影响的示意图^[14]

Fig. 1 Schematic diagram of the effect of trapped ions on the OCP and charge density of inserted ions^[14]

物理制备方法, 北京航空航天大学刁训刚课题组^[18]采用磁控溅射法研究了 WO₃ 薄膜在 Ar 和 O₂ 气氛中退火后的性质, 如图 2 所示, 发现在 Ar 气中氧空位浓度高, WO₃ 薄膜的 EC 性能更好, 但循环稳定性变差。

1.3.2 元素掺杂

图 3 展示了 2016~2020 年已研究的 WO₃ 薄膜掺杂元素在元素周期表中的分布。Co^[19]、Ni^[20]、Mo^[21-22]、Nb^[23]、Ti^[24-25]、Ru^[26]、Au^[27]、Li^[28]、Sb^[29] 等金属元素掺杂和 Eu^[30-31]、Gd^[32]、Tb^[33]、Ce^[34] 等稀土元素掺杂能明显增强 WO₃ 薄膜的 EC 性能, 有些元素甚至还表现出其他的功能。中国科学技术大学徐春叶课题组^[19]发现 Co 离子掺杂的 WO₃ 膜表面形貌变化显著, 表现出更高的透射率调制(680 nm 处 75.4%)和超过 4000 次的稳定性。该课题组还通过水热法将 Tb 离子掺杂到 WO₃ 薄膜中^[33], 抑制了 WO₃ 的定向生长, 引入的非晶态和多孔网状结构使 WO₃ 薄膜具有良好的 EC 性能, 同时 WO₃ 薄膜还具有光致发光的功能, 可以在 260 nm 紫外光下实现绿

色发射。浙江大学涂江平课题组^[23]研究了 Nb 掺杂的 WO₃ 薄膜, 具有超快的响应速度, 着色和漂白时间分别为 3.6 和 2.1 s。

1.3.3 纳米结构

纳米结构是通过改变薄膜物理形貌来增大薄膜与电解质之间的接触面积, 从而达到缩短电荷传输距离的目的。设计纳米点、纳米线、纳米棒和纳米片等低维纳米结构已被证明是提高 WO₃ 薄膜电致变色性能的有效策略, 快速的离子/电子转移速度和更多的活性位点有助于增强 WO₃ 薄膜的光学调制程度和缩短着褪色响应时间。

上海大学高彦峰课题组^[35]报道了具有 97.8% 的超大光调制范围和 20000 次长循环寿命的 WO₃ 量子点薄膜。刁训刚等^[36]采用电沉积法制备了具有二维网格结构的 WO₃ 薄膜, 着色和漂白时间极短(1.27 和 0.93 s), 比平面 WO₃ 薄膜(2.34 和 2.18 s)快得多, WO₃ 薄膜结构见图 4。浙江大学韩高荣课题组^[37]采用湿化学方法成功地制备了尺寸可调的电致变色 WO₃ 纳米棒, WO₃ 纳米棒的平均长度和直径可从

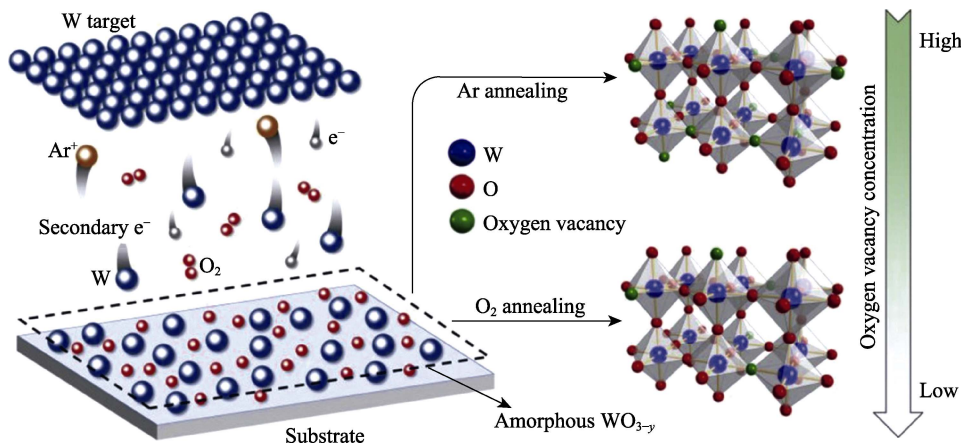


图 2 WO₃ 薄膜的制备过程、晶体结构和氩/氧气氛退火引起的氧空位变化^[18]

Fig. 2 Illustration of WO₃ thin films fabrication process, crystal structure and oxygen vacancy change induced by Ar/O₂ atmosphere annealing^[18]

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr			

图 3 2016~2020 年已研究 WO₃ 和 NiO 薄膜的掺杂元素

Fig. 3 Elements doped to WO₃ and NiO films which researched from 2016 to 2020

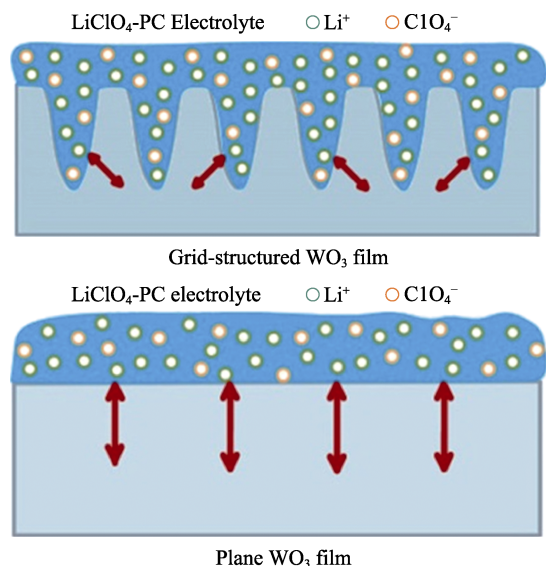


图 4 2D 网格结构和平面 WO_3 膜的电致变色机理图^[36]
Fig. 4 Electrochromic mechanism diagram of 2D grid-structured and plane WO_3 film^[36]

38 nm×3.2 nm 增加到 89 nm×4.5 nm, 简单地改变纳米棒的尺寸, 薄膜的响应速度可以提高近 5 倍。

1.3.4 复合材料

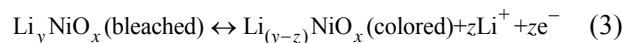
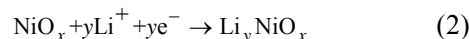
由于材料的固有特性, 单一的电致变色材料往往无法兼顾高的电致变色性能和长期稳定性, 利用复合材料的协同作用可以使材料获得更加丰富的功能, 如将有机和无机材料结合可以同时获得丰富的颜色变化、快速的切换时间和良好的循环稳定性。哈尔滨工业大学李焱等^[38]采用溶剂热法和电聚合合法制备了 $\text{WO}_3@\text{PANI}$ 海胆状结构的复合材料, 表现出紫色、绿色、黄色、灰色、蓝色等多种颜色变化, 长期循环性能优异。青岛科技大学聂广明课题组^[39]制备的聚(5-甲酰基咪唑)/ WO_3 蜂窝孔状纳米复合材料能在深绿色、黄色和黄绿色之间可逆切换, 着色效率高达 $137 \text{ cm}^2/\text{C}$ 。

2 NiO 薄膜研究进展

2.1 NiO 的结构和变色机制

NiO 晶体是 NaCl 型面立方结构, 在实际制备时 NiO 薄膜通常为非化学计量比的 P 型半导体, 存在 Ni^{2+} 空位。 NiO 在碱性溶液和在含 Li^+ 电解液等不同类型电解质中的电致变色机制完全不同。在碱性溶液如 KOH 中的变化可参考 Bode 模型^[40], NiO 的变色过程是从透明的 $\text{Ni}(\text{OH})_2$ 转化到有色 NiOOH , 光谱吸收与 Ni^{2+} 和 Ni^{3+} 之间的电荷转移有关。Passerini 等^[41]初步提出了 NiO 薄膜在 $\text{LiClO}_4\text{-PC}$ 中的变色机制, 首先 NiO 通过不可逆反应变成透明的

Li_yNiO_x , 然后 Li^+ 离子和电子的共同嵌入脱出使 Li_yNiO_x 和 $\text{Li}_{(y-z)}\text{NiO}_x$ 之间发生可逆的颜色转换, 如式(2)和(3)。



另外还有研究表明 NiO 薄膜的变色与薄膜表面离子有关以及在电致变色过程中生成了更高价态的 Ni^{4+} , 这些理论进一步完善了 NiO 的电致变色机制。

2.2 NiO 薄膜的衰退机制

WO_3 和 NiO 组成的互补型电致变色器件的循环寿命在很大程度上受到 NiO 薄膜衰退的限制。对于 NiO 在碱性电解质中的衰退机制, Bouessaya 等^[42]认为是 $\text{Ni}(\text{OH})_2$ 发生自放电导致薄膜被部分降解。 NiO 在含 Li^+ 的非水电解质中的衰退与 WO_3 相似, Li^+ 被“深陷阱”捕获导致不可逆脱出, 增加了离子扩散阻力, 从而使 NiO 薄膜性能下降。刁训刚等^[43]利用聚焦离子束切割器结合二次离子质谱实验研究了 NiO 薄膜在无机全固态器件中的退化情况, 发现不可逆捕获的 Li^+ 在 NiO 薄膜中累积, NiO 薄膜结构从疏松变得致密。

2.3 NiO 薄膜的性能优化

氧化镍在褪色时为透明态或浅褐色, 着色时呈现深棕色, 这种柔和的中性色可与 WO_3 的颜色叠加, 非常适合用于智能窗中。但是 NiO 的光学调制率通常不如 WO_3 , 还存在漂白态的透过率较低、着褪色响应时间长、长期循环稳定性差等问题。本节从薄膜的生产方法改进、元素掺杂、纳米结构的设计和复合材料的引入等方面介绍 NiO 电致变色性能优化的研究进展。

2.3.1 制备方法

同 WO_3 的制备方法类似, NiO 的制备主要有旋涂^[44]、水热^[45-46]、溶胶-凝胶^[47]、电沉积^[48]和溅射^[49]等方法。严辉等^[50]采用溶胶-凝胶法制备了 NiO 薄膜, 并研究了退火温度对 NiO 薄膜的影响, 经 $350 \text{ }^\circ\text{C}$ 退火的 NiO 薄膜具有 50.7% 的透过率调制范围和 $71.4 \text{ cm}^2/\text{C}$ 的着色效率。李焱等^[51]通过连续改变磁控溅射时的基底温度, 制备了一种晶体结构从有序到无序连续变化的 NiO 薄膜, 如图 5 所示, 这种 NiO 薄膜很好地兼顾了优异的 EC 性能和良好的循环稳定性。

2.3.2 元素掺杂

近期对氧化镍薄膜元素掺杂的研究集中在金属元素掺杂, 如 Cu ^[52]、 Li ^[53]、 W ^[54] 和 Li-Mg ^[55]、 Li-Ta ^[56] 双元素共掺杂等, 见图 3。Firat 等^[52]研究了 Cu 掺杂

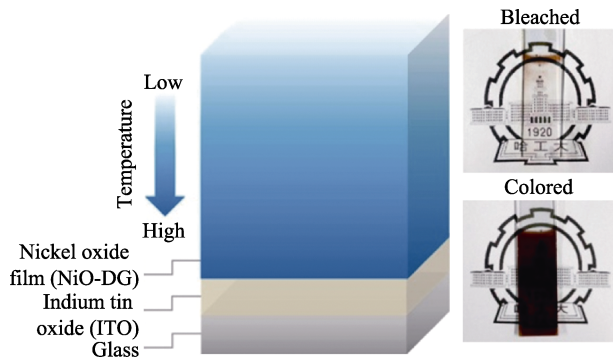


图 5 结晶度梯度变化的 NiO 薄膜和着褪色态照片^[51]

Fig. 5 Schematic of the crystallinity gradient in NiO film and photos of NiO film in colored and bleached state^[51]

NiO 薄膜的形貌和 EC 性能, Cu 掺杂的 NiO 薄膜具有极短的颜色响应时间, 着色为 1.77 s, 褪色为 2.26 s。Lee 等^[54]采用直流反应磁控溅射法, 以钨镍合金为靶材制备了 W 掺杂的 NiO 薄膜, W 掺杂能使纯 NiO 膜在电化学循环过程中由深陷阱位点引起的退化降至最低。刁训刚等^[55]使用射频磁控溅射法在 NiO 薄膜中共掺杂了 Mg 和 Li, 通过预锂化扩大了 NiO 的间隙, 改善了短波长下 NiO 薄膜的 EC 性能。

2.3.3 纳米结构

设计纳米结构的 NiO 可以缩短离子的扩散距离, 提高 NiO 薄膜的响应速度, 多孔纳米结构还能离子传输提供通道, 有效提高 NiO 薄膜的循环稳定性。Wu 等^[57]使用电泳沉积法制备了晶粒尺寸在 10.36 nm 左右的 NiO 纳米晶薄膜, 在 550 nm 处具有较大的光调制幅度(54.1%), 切换速度较快($t_c=7.3$ s, $t_b=3.9$ s)。如图 6 所示, 李焱等^[58]报道了一种简便 ZnO 模板辅助水解法制备的 NiO 纳米管阵列膜, 具有极大的透过率调制(78.5%)和快速的开关响应时

间($t_c=3.92$ s, $t_b=3.43$ s)。Ren 等^[59]采用光敏溶胶-凝胶法制备了多孔阵列的 NiO 图案膜, 与致密的 NiO 膜相比, 多孔 NiO 图案膜具有更好的电致变色性能和更长的使用寿命(3000 次)。

2.3.4 复合材料

NiO 薄膜的低导电性导致了开关速度慢、着色效率低的问题, 利用复合材料的协同作用可以改善 NiO 薄膜的电致变色性能。中国科学院长春光学精密机械与物理研究所刘星元团队^[60]采用简单的一步电子束沉积法, 在室温条件下成功地制备了透明、导电、无需 ITO 的 NiO/Ag/NiO 膜, 该薄膜在可见光区平均透过率超过 70%。东华大学王宏志课题组^[61]通过金属有机骨架(MOF)的两步热解法制备了分级多孔 NiO@C 薄膜, 制备流程见图 7, 调节 C 的含量可改善薄膜的电化学和 EC 性能, 最佳 C 含量的多孔 NiO@C 薄膜具有极快的切换速度($t_c=0.46$ s, $t_b=0.25$ s)、超高的着色效率(113.5 cm²/C)和显著的循环稳定性 20000 次)。

3 基于 WO₃ 和 NiO 的电致变色器件

传统的电致变色器件为五层结构, WO₃ 和 NiO 通常作为电致变色层和离子存储层, 二者中间是离子传导层, 两侧是用于传输电子的透明导电层。电致变色器件的整体性能不仅与各层薄膜的性质有关, 还取决于层与层之间的协同作用和器件结构的设计。

3.1 透明导电层

透明导电层是电致变色器件的重要组成部分, 起到连接器件与外电路的作用。常见的透明导电薄膜包括金属薄膜和金属氧化物半导体膜, 在智能窗

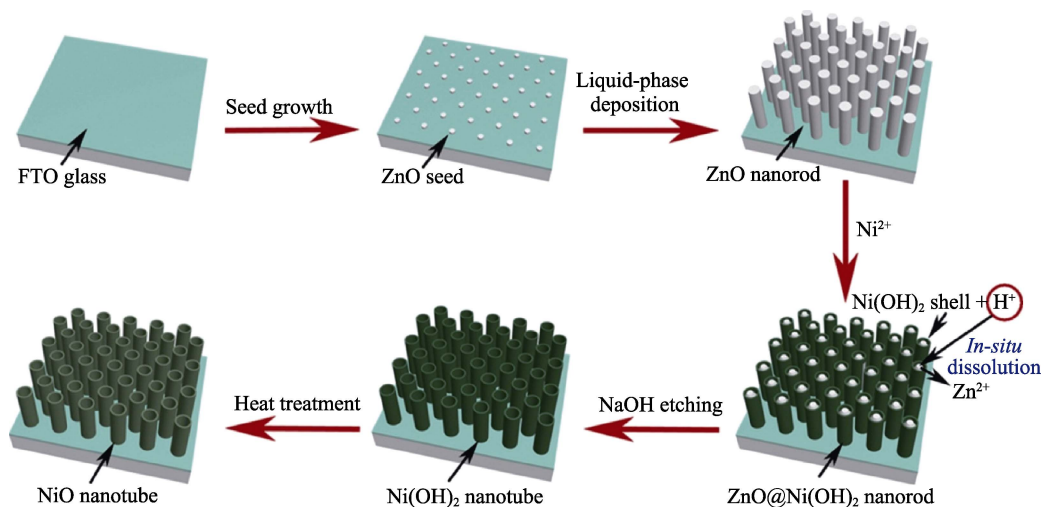
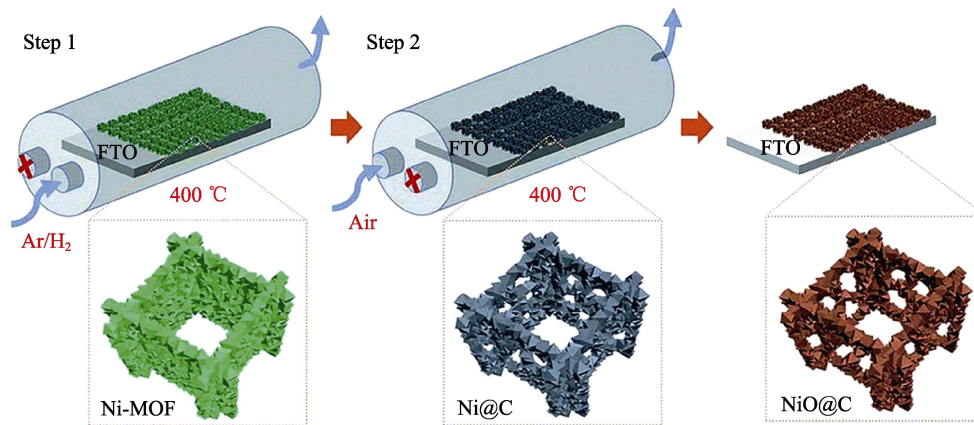


图 6 NiO 纳米管阵列的制备示意图^[58]

Fig. 6 Facile preparation of aligned NiO nanotube arrays^[58]

图 7 多孔分层 NiO@C 薄膜的制备示意图^[61]Fig. 7 Preparation procedures of the hierarchical-porous NiO@C film^[61]

等应用中要求透明导电膜同时具有高透过率和高导电性。金属虽然具有良好的导电性,但是在可见光波段不透明,极薄的金属膜可以解决透光问题,然而制备较为困难,容易引入不连续的岛状结构,反而增加电阻率。金属氧化物薄膜因在可见光区具有很好的透过性而被广泛使用,常见的有 $\text{In}_2\text{O}_3:\text{Sn}$ (ITO), $\text{SnO}_2:\text{F}$ (FTO)和 $\text{ZnO}:\text{Al}$ (AZO)等。

ITO的研究和应用最多,ITO不仅具有较低的电阻率和高可见光透过率,还具有与基底结合牢固、抗擦伤的优点。然而单层的ITO存在电导率与透过率难以平衡的问题,因此一种新的“电介质/金属/电介质”三层结构透明导电膜得到了人们的关注。刁训刚等^[62]采用磁控溅射法在玻璃基底上制备了具有低电阻和高透明性的堆叠ITO/Ag/ITO(IAI)电极。IAI(50 nm/5 nm/30 nm)薄膜的薄层电阻低至 7.4Ω ,在 NiO_x 、 WO_3 电致变色薄膜和完整的 Glass/IAI/ $\text{NiO}_x/\text{LiClO}_4\text{-PC-PMMA}/\text{WO}_3/\text{IAI}/\text{Glass}$ 器件中均表现出优异的性能。为了解决ITO导电薄膜中In元素稀少、有毒造成的高成本和污染性的问题,该课题组还研究了AZO薄膜的性能^[63],其品质因数高达 $12.14 \times 10^{-3} \Omega^{-1}$,平均透射率为 92.2%,但AZO的电学性能还有待提高。

另外,具有高机械稳定性的柔性透明导电膜的研究也备受关注。刁训刚等^[64]采用磁控溅射法在柔性透明PET基底上沉积ITO薄膜,并继续逐层沉积 $\text{NiO}_x/\text{LiTaO}_3/\text{WO}_3/\text{ITO}$ 制成了柔性无机电致变色器件,具有较高着色效率($68.5 \text{ cm}^2/\text{C}$)。由于ITO本身的刚性限制,在柔性基底上制备的ITO薄膜效果不佳,许多新的柔性透明导电材料如金属纳米线、金属网格^[65]、石墨烯、碳纳米管和PEDOT:PSS^[66-67]等导电聚合物已经得到广泛研究,并有希望成为ITO的替代品。

3.2 离子传导层

在互补型电致变色器件中,离子传导层位于阴极和阳极电致变色材料中间,起到提供变色阳离子和阻隔电子的作用。离子传导层通常选用高离子电导率、低电子电导率的透明电解质,包括液态电解质、凝胶电解质和固态电解质。

液态电解质的离子迁移率最高,能为电致变色器件提供快速的可逆反应,北京航空材料研究院颜悦团队^[68]分别研究了 LiClO_4 、 LiPF_6 、 LiTFSI 三种含有不同锂盐的液体电解质对 NiO 、 WO_3 薄膜和 Glass/ITO/ $\text{WO}_3/\text{Li}^+/\text{NiO}/\text{ITO}/\text{Glass}$ 结构电致变色器件的影响,不同电致变色膜在同一电解液中的电压和阻抗具有明显差异。液态电解质虽然具有优异的离子电导率,但其腐蚀性和流动性往往造成封装上的困难和漏液风险,构建多孔结构的离子传导层或引入吸附毡均是比较有效的解决策略。

凝胶电解质由于透明度高、导电性好和机械稳定性优异的特点而备受青睐,可用于柔性器件中,如 PMMA-LiClO_4 等。苏州纳米所赵志刚等^[69]研制了一种新型的独立芳纶纳米纤维凝胶聚合物电解质,具有良好的耐热性和成膜能力,利于 WO_3 和 NiO 电致变色器件的组装。Wootthikanokkhan 等^[70]将明胶、乙烯-丙烯酸共聚物离聚物树脂(EAA)与甘油、 LiClO_4 、甲醛等混合制成凝胶电解质,实现了很高的离子电导率($4.46 \mu\text{S}/\text{cm}$)。

固态电解质具有良好的稳定性和耐候性,便于封装和大规模制备,在全固态电致变色器件中具有极其重要的地位,如 Ta_2O_5 ^[71]、 ZrO_2 ^[72]、 LiF ^[73]、 LiPON ^[74]等。锂离子固态电解质的研究较为成熟,李焱课题组^[73]采用电阻蒸发法制备了 LiF 无机固态电解质,在无机全固态 glass/ITO/ $\text{WO}_3/\text{LiF}/\text{NiO}/\text{ITO}$ 器件中表现出良好的性能。中国科学院上海硅酸盐研

究所包山虎团队^[75]通过锂铝靶共溅射制备出的 Li_xAlO_2 薄膜具有高透明度、良好的离子导电性和超高稳定性, 该团队还制备了 $10\text{ cm}\times 10\text{ cm}$ 的大型全固态电致变色器件($\text{ITO}/\text{NiO}_x/\text{Li}_x\text{AlO}_2/\text{WO}_3/\text{ITO}$), 如图 8 所示。固态电解质在应用和制备上具有独特的便捷性, 但是离子电导率低的问题仍是当前固态电解质的研究重点。

3.3 器件结构设计

WO_3 和 NiO 薄膜组成的电致变色器件通常具有标准的“三明治”结构, 离子传导层中的阳离子在电场的作用下会从 NiO 薄膜中脱出并嵌入到 WO_3 薄膜中, 使 WO_3 和 NiO 电致变色膜同时着色, 反之二者同时褪色。表 1 总结了近五年来由 WO_3 和 NiO 组成的电致变色器件的结构与响应时间(t_c 、 t_b)、着色效率(CE)和光调制范围(ΔT)等性能对比。

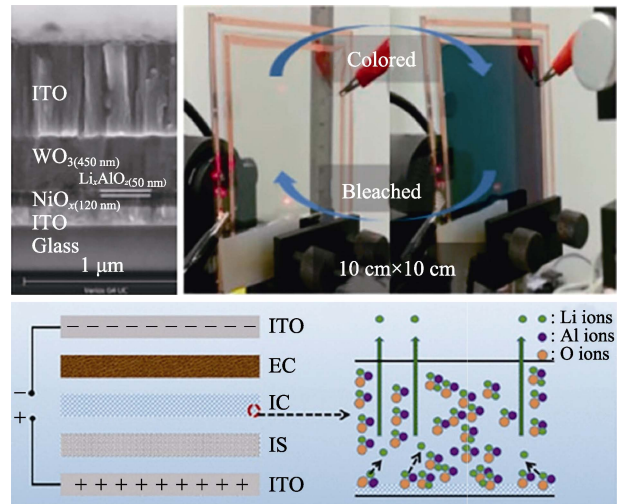


图 8 大型全固态器件结构示意图和照片^[75]
Fig. 8 Schematic diagram of large-scale all-solid-state device structure and photograph^[75]

表 1 2016~2020 年基于 WO_3 和 NiO 薄膜的电致变色器件结构与性能对比

Table 1 Comparison of structure and performance of ECDs based on WO_3 and NiO films researched from 2016 to 2020

Year	Device structure	t_c/s	t_b/s	CE/($\text{cm}^2\cdot\text{C}^{-1}$)	$\Delta T/\%$	Cycles	Ref.
2016	ITO/ $\text{NiO}_x/\text{ZrO}_2/\text{H}/\text{WO}_3/\text{ITO}$	116	108	-	65.2	2000	[72]
2016	ITO/ $\text{NiO}_x/\text{Ta}_2\text{O}_5/\text{H}/\text{WO}_3/\text{ITO}$	-	-	-	60	-	[76]
2016	ITO/ $\text{WO}_3/\text{LiClO}_4\text{-PC-PMMA}/\text{NiO}_x/\text{ITO}$	4.5	1.7	-	51.7	50000	[77]
2016	Glass/ITO/ $\text{WO}_3/\text{LiNbO}_3/\text{NiO}_x/\text{ITO}$	45	25	-	65	-	[78]
2016	ITO/ $\text{NiO}_x/\text{Ti}/\text{PVB}(\text{Li}^+)/\text{WO}_3/\text{ITO}$	4.4	3.2	96	60	-	[79]
2017	Glass/ITO/ $\text{WO}_3/\text{PVB-GPEF}/\text{Ni}_{1-x}\text{O}/\text{ITO}/\text{Glass}$	9.5	16	175.34	65.8	3000	[80]
2017	Glass /ITO/ $\text{NiO}_x/\text{electrolyte}/\text{WO}_3/\text{ITO}$	7	2	-	70	300	[81]
2017	Glass /ITO/ $\text{NiO}/\text{Si}_3\text{N}_4/\text{LiNbO}_3/\text{Si}_3\text{N}_4/\text{WO}_3/\text{ITO}$	-	-	-	43	-	[82]
2017	ITO/ $\text{NiO}/\text{Ta}_2\text{O}_5/\text{LiNbO}_3/\text{WO}_3/\text{ITO}$	-	-	-	34	-	[83]
2018	Glass/ITO/ $\text{NiO}/\text{Si}_3\text{N}_4/\text{Li}_x\text{Mg}_y\text{N}/\text{WO}_3/\text{ITO}$	-	-	77	40	1000	[84]
2018	Glass/ITO/ $\text{WO}_3/\text{Li}_{2.5}\text{TaO}_x/\text{NiO}/\text{ITO}$	30	30	63	40	300	[71]
2018	FTO/ $\text{WO}_3/\text{gel polymer electrolyte}/\text{NiO}/\text{FTO}$	1.2	2.6	-	43.81	20000	[85]
2018	Glass/ITO/ $\text{WO}_3/\text{H}/\text{Ta}_2\text{O}_5/\text{NiO}_x/\text{ITO}$	-	-	24.3	42	300	[86]
2018	Glass/ITO/ $\text{WO}_3/\text{LiPON}/\text{NiO}/\text{ITO}$	-	-	-	40	-	[74]
2018	Glass/ITO/ $\text{Li}_x\text{NiO}_y/\text{LiTaO}_3/\text{WO}_3/\text{ITO}$	13	3.5	42	40	7000	[87]
2018	ITO/ $\text{NiO}_x/\text{Ta}_2\text{O}_5/\text{LiNbO}_3/\text{Ta}_2\text{O}_5/\text{WO}_3/\text{ITO}$	-	-	98	52.5	10000	[88]
2018	ITO/ $\text{NiO}/\text{ZrO}_2/\text{LiNbO}_3/\text{WO}_3/\text{ITO}$	-	-	24.3	53	-	[89]
2018	ITO/ $\text{NiO}/\text{Ta}_2\text{O}_5/\text{LiNbO}_3/\text{WO}_3/\text{ITO}/\text{Glass}$	10	7	-	71.7	-	[90]
2019	Glass/IAI/ $\text{NiO}_x/\text{LiClO}_4\text{-PC-PMMA}/\text{WO}_3/\text{IAI}/\text{Glass}$	2.25	2.02	31.7	55	-	[62]
2019	ITO/ $\text{NiO}_x/\text{Li}_x\text{AlO}_2/\text{WO}_3/\text{ITO}$	5.7	2.2	76.45	74.4	10000	[75]
2019	ITO/ $\text{WO}_3\text{-Nb}_2\text{O}_5/\text{Nb}_2\text{O}_5/\text{NiVO}_x/\text{ITO}$	7	0.7	-	33	30000	[91]
2019	ITO/ $\text{WO}_3/\text{LiClO}_4\text{-PC-PMMA}/\text{NiO}/\text{ITO}$	3.2	1.1	130.8	45	1000	[92]
2019	ITO/ $\text{NiO}_x/\text{Ta}_2\text{O}_5/\text{LiNbO}_3/\text{Ta}_2\text{O}_5/\text{WO}_3/\text{ITO}$	18.4	9.5	-	55.2	2500	[93]
2019	ITO/ $\text{NiO}_x/\text{Ta}_2\text{O}_5/\text{WO}_3/\text{ITO}$	13	2	-	70.9	-	[94]
2020	Glass /ITO/ $\text{WO}_3/\text{LiF}/\text{NiO}/\text{ITO}$	9.6	4	88.5	58.9	450	[73]
2020	ITO/ $\text{WO}_3/\text{Gelatin}/\text{NiO}/\text{ITO}$	10	50	60.38	43.35	-	[70]
2020	ITO/ $\text{Li-NiO}/\text{Li-WO}_3/\text{ITO}$	8.6	1.7	87.5	32	1000	[95]
2020	ITO/ $\text{WO}_3/\text{LiClO}_4\text{-PC-PMMA-ACN}/\text{NiO}/\text{ITO}$	1.2	1.5	243	51.27	20000	[96]
2020	ITO/ $\text{WO}_3/\text{LiNbO}_3/\text{Al-LiNiO}_x/\text{ITO}$	17.9	4.1	-	44	5000	[97]

一个标准的 ECD 由透明导电层、电致变色层、离子传导层、离子存储层和透明导电层五部分组成,按制备方式的不同又可分为单片式和夹层式两种结构。单片式通常是采用磁控溅射法在基底上连续沉积多层薄膜,离子传导层为陶瓷等无机固态电解质,这种结构由于各膜层均是固体又被称为全固态电致变色器件,如图 9(a)所示。夹层式的 ECD 是先在两玻璃基底上分别制备 WO_3 和 NiO 薄膜,再通过层压、胶合等方式组装成器件,如图 9(b)所示,这是一种简便的组装方式,液态电解质或凝胶电解质均可用于夹层式 ECD 中。

刁训刚等^[71]采用磁控溅射法在单层的 ITO 玻璃上连续溅射沉积制备了单片式电致变色器件(Glass/ITO/ WO_3 / $\text{Li}_{2.5}\text{TaO}_x$ / NiO /ITO),并研究了 $\text{Li}_{2.5}\text{TaO}_x$ 厚度对器件的影响。该课题组还制备了 ITO/ WO_3 / LiClO_4 -PC-PMMA/ NiO_x /ITO 夹层式结构的全固态电致变色器件^[77],具有超过 50000 次的超高循环耐久性。

电解质层阻挡电子的能力较差,容易造成器件漏电流和差的光学记忆效应,因此人们在五层结构 ECD 的基础上提出了七层结构器件,如图 9(c)所示。在电解质层两侧增加保护层如 ZrO_2 ^[98]、 Ta_2O_5 ^[88] 等,可以使器件获得更高的着色效率、更好的光记忆效果和更长的循环寿命,但响应速度和透光率会因此受到一定影响。刁训刚等^[88]制备了七层结构 ECD(ITO/ NiO_x / Ta_2O_5 / LiNbO_3 / Ta_2O_5 / WO_3 /ITO),相比于无 Ta_2O_5 保护的五层结构器件来说具有低漏电流、 $98 \text{ cm}^2/\text{C}$ 的高着色效率和 10000 次循环寿命。

锂化是一种常见的提升薄膜电致变色性能的手段,将 Li^+ 引入到电致变色薄膜中替代电解质是一

种新的器件结构设计思路,李焱等^[95]提出了一种四层结构 ITO/ Li-NiO / Li-WO_3 /ITO 全固态电致变色器件,将 Li^+ 直接蒸发在 WO_3 和 NiO 薄膜上,取代了传统结构中的离子传导层,如图 9(d)所示, Li^+ 直接在 WO_3 和 NiO 层之间转移使得器件的总电阻变低,响应速度变快,但这种结构对器件光调制幅度和稳定性的影响还有待进一步的研究。总之,每种器件结构都有其独特的优势,并由各组成成分的综合性能决定,在实际生产设计时应针对不同的应用场景和使用需求选择合适的组分和器件结构。

4 结论与展望

本文综述了基于 WO_3 和 NiO 的电致变色器件近年来的研究进展,重点讨论了电致变色层 WO_3 和离子存储层 NiO 薄膜的研究现状,总结了器件其他组分和组装方式发挥的作用和典型器件性能对比。基于 WO_3 和 NiO 的电致变色器件具有驱动电压低和双稳态的性能,在节能领域尤其是智能窗的应用中已趋于成熟,目前美国 Sage-Glass、View Inc.、德国 EControl-Glas 以及瑞典 Chromo Genics 等多家公司均可实现电致变色玻璃的大规模工业化生产。但国内的大多数研究还处于实验室或中试阶段,在智能窗的生产尤其是在提高大尺寸全器件的稳定性和完善工艺等方面仍然面临着巨大的挑战,虽然近几年国内的学者们已经对此做了诸多努力,但大都集中在改善单层薄膜性能的研究上,缺乏对电致变色全器件的持续研究,进一步探究全器件的性能和突破工业生产的技术瓶颈仍是当前的研究重点。除了智能窗以外,工作温度范围宽、化学稳定性好、循环寿命长等优点使电致变色器件也非常适合用于室外环境,目前已有许多学者致力于开发电致变色器件在电子领域的应用,特别是在静态图像显示、户外广告、仪表显示等领域的前景可待。

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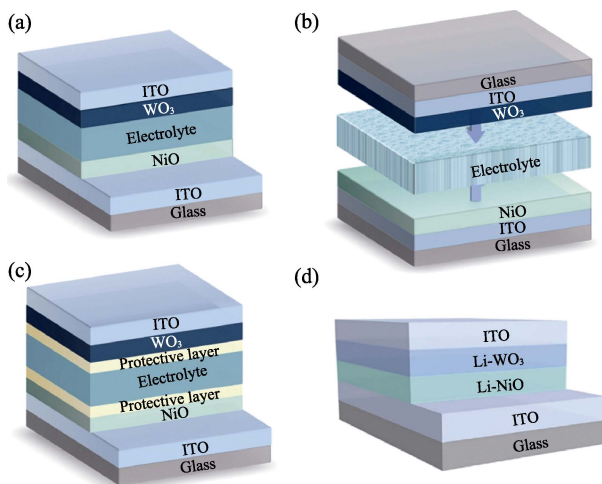


图 9 ECD 的结构示意图

Fig. 9 Structural schematic diagram of ECD

(a) Monolithic ECD; (b) Laminated ECD; (c) Seven-layered ECD; (d) Four-layered ECD^[95]

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