

基于溶胶-凝胶法制备的离子导体层的电致变色器件及性能

苏文敬^{1,2}, 王天齐^{1,2}, 金克武^{1,2}, 汤永康^{1,2}, 沈洪雪^{1,2}, 李 刚^{1,2}

(1. 中建材玻璃新材料研究院集团有限公司, 先进玻璃材料全国重点实验室, 安徽 蚌埠 233018;

2. 安徽省硅基材料实验室, 安徽 蚌埠 233018)

摘 要: 开发了离子导体材料钽酸锂的溶胶-凝胶法合成工艺并采用旋涂法制备了钽酸锂薄膜, 采用 X 射线衍射仪、原子力显微镜及电化学工作站等对薄膜进行了物相形貌及电化学性能表征。其中溶胶-凝胶法制备的钽酸锂薄膜室温离子电导率可以达到 $7.44 \times 10^{-7} \text{ S/cm}$ 。采用旋涂法分别在 ITO/NiO 和 ITO/ WO_3 基底上制备了钽酸锂薄膜, 并采用磁控溅射法制备相应的电致变色层和离子存储层及透明导电电极, 通过液相法与 PVD 法结合制备出了结构为 ITO/NiO/LiTaO₃/ WO_3 /ITO 的电致变色器件, 研究发现以 ITO/NiO 为基底旋涂钽酸锂制备的电致变色器件具有较高的变色幅度和较快的转变速率, 在施加 5 V 外加电压时, 可见光调节幅度可以达到 26%, 着色时间约为 50 s, 褪色时间为 56 s。而在氧化钨薄膜表面旋涂钽酸锂制备的器件对近红外波段有较好的调控, 但是相同电压下器件褪色和着色速率大幅下降, 相同电压下可见光调节幅度也有所降低。

关键词: 溶胶-凝胶法; 锂离子导体层; 电致变色; 全固态无机电致变色器件; 局域表面等离子体共振; 近红外波段调控

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电致变色是一种对材料施加电压时会可逆地改变其光学透过率性能的现象, 当施加一个方向的电压时器件透过率会降低, 称为着色态。改变电压方向, 器件变得透明, 称为褪色态。电致变色器件是基于材料的电致变色现象将不同功能膜层集成制备的器件, 随着外加电压极性的改变可以在褪色态和着色态之间循环往复。1969 年 Deb 首次发表了关于钨的氧化物的电致变色的工作^[1], 随后在 1973 年详细描述并解释了这一现象^[2]。Deb 关于氧化钨变色的工作开创了电致变色器件研究的先河。

早期关于电致变色的研究的主要是为了用于显示^[3-7]。1980 年代的研究发现电致变色材料用于玻璃窗可具有节能的效果^[8-9], 随后科学家提出了基于电致变色的智能窗的概念^[10-11], 掀起了电致变色研究的又一波热潮。目前电致变色器件的可见光调节幅度可达到 60% 以上, 变色所需时间通常在 1~10 min 之间^[12], 在建筑、汽车天窗等领域已经有了很好的应用。随着碳中和及更高的节能舒适性要求, 人们越来越多的关注电致变色器件对光和热的双调节, 可见和近红外双波段调节的电致变色器件成为当前研究的一个热点^[13-15]。

电致变色器件通常由五层叠加的膜层组成, 其中包括两层透明导电层及夹在其间的电致变色层、离子导体层和离子存储层。根据电致变色层材料性质可以分为有机电致变色器件与无机电致变色器件, 其中由过渡金属氧化物及无机固态电解质膜层组成的无机全固态电致变色器件具有高的化学、热稳定性和长的循环寿命, 在建筑等室外环境下最具应用潜力。

电致变色器件的制备通常有磁控溅射法^[16-19]、化学气相沉积法^[20-23]、溶胶-凝胶法^[24-26]等, 其中溶胶-凝胶法能精准控制薄膜材料的化学组分, 对膜层进行掺杂改性。此外, 溶胶-凝胶薄膜热处理温度相对较低^[27], 可以可控制备出具有不同纳米结构的薄膜, 且制备的膜层具有很高的均匀性。例如, 采用溶胶-凝胶法可以制备出具有多孔结构的薄膜, 以缩短离子迁移的距离^[24-26], 提升电致变色器件的性能。针对电致变色器件中的不同金属氧化物膜层, 目前都有大量关于溶胶-凝胶法的制备研究, 如阴极电致变色材料 WO_3 ^[26-34]、 MoO_3 ^[35] 和 TiO_2 ^[36], 阳极电致变色材料 NiO ^[37-40]、 CoO_3 ^[41] 及 CeO_2 ^[42] 等。而对于其中固态电解质层的溶胶-凝胶法制备报道较

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第一作者: 苏文敬(1987), 男, 硕士, 高级工程师。

Received date: 2025-03-24. Revised date: 2025-04-17.

First author: SU Wenjing (1987-), male, Master, Senior Engineer.

E-mail: 281226975@qq.com

少。钽酸锂(Lithium tantalite, LiTaO_3)作为一种固态电解质材料,常用于无机全固态电致变色器件的离子导体层^[43–45],然而传统的磁控溅射法制备的薄膜沉积速率慢且材料利用率低,增加了器件成本。

本工作采用溶胶–凝胶法制备了钽酸锂溶胶,并且对其薄膜制备及性能进行了研究。通过与物理气相沉积(PVD)法结合,制备出了结构为ITO/NiO/ LiTaO_3 / WO_3 /ITO的电致变色器件。对器件的性能测试发现基于氧化镍表面旋涂 LiTaO_3 薄膜制备的电致变色器件与基于氧化钨表面旋涂相应膜层制备的器件性能有显著差异,其中以氧化镍膜层为基底旋涂薄膜制备的器件透过率调节幅度及褪色和着色速率等性能较优,而以氧化钨膜层为基底旋涂制备的器件对近红外波段的调控效果更加显著。

1 实验

1.1 钽酸锂溶胶的合成与薄膜的制备

采用无水醋酸锂和乙醇钽为合成原材料,溶剂为1,2-丙二醇。将无水醋酸锂与1,2-丙二醇以物质的量比1:50加入溶剂中,在130℃加热回流并搅拌3 h,随后冷却至60℃,并滴加无水醋酸将混合溶液pH值调至5左右,采用移液管将与无水醋酸锂摩尔比为1:1的乙醇钽加入混合溶液,升温至130℃后持续回流24 h。回流完成的溶液在室温静置陈化备用。然后取部分溶胶烘干得到粉末,在600~700℃退火2 h,对粉末进行X射线衍射(XRD)测试。

采用旋涂镀膜法制备 LiTaO_3 薄膜,旋涂镀膜的工艺参数为:匀胶300 r/min,时间15 s;甩胶3000 r/min,时间45 s。旋涂完每层湿膜后,在150℃的烘箱中干燥5 min,然后200℃高温炉中干燥灼烧5 min,以进行下一层旋涂。重复上述过程以制备出满足所需厚度的薄膜。完成所有膜层的旋涂后在400℃对薄膜进行热处理2~4 h。

1.2 电致变色器件的制备

采用反应磁控溅射法在方阻约10 $\Omega/\square$ 的ITO/Glass(可见光平均透过率~84%)基底上分别制备氧化钨、氧化镍薄膜,在氧化钨或氧化镍薄膜表面上旋涂制备钽酸锂薄膜,完成后在400℃空气气氛中热处理2 h,然后利用反应磁控溅射制备相应的另一层氧化镍或氧化钨薄膜,并溅射沉积ITO透明电极。

1.3 性能测试

采用Bruker D8 Advance型X射线衍射仪对溶胶–凝胶粉末及薄膜进行物相分析,采用Thermo Scientific ESCALAB 250Xi型X射线光电子能谱仪(XPS)进行表面原子能谱测试,采用FEI Nova NanoSEM450场发射扫描电子显微镜(SEM)测试薄膜断面厚度,采用Autolab PGSTAT302N+ECI MSPP MULTIPLEX XDM-100M对薄膜进行电化学阻抗谱测试及循环伏安(Cyclic voltammetry, CV)和计时电流(Chronoamperometry, CA)测试,循环伏安的测试电压为-2 V到+2 V,扫描速率为10 mV/s。采用Bruker Dimension icon原子力显微镜(AFM)进行表面形貌和粗糙度测试,采用Hitachi U4100分类光度计进行透过率测试。对电致变色器件,在进行计时电流扫描的同时进行透过率曲线测试,计时电流着色态测试电压为-2 V至-5 V,扫描时间为90~240 s,褪色态测试电压为+2 V至+4 V,扫描时间为60~120 s。循环扫描透过率为550 nm固定波长时测试结果。

2 结果与讨论

2.1 钽酸锂的粉末及薄膜的物相和组分分析

钽酸锂溶胶干燥后的粉末在600℃热处理2 h。粉末的XRD谱如图1a所示。通过衍射峰的分析,表明粉末为 LiTaO_3 多晶粉末。对于旋涂制备得到的

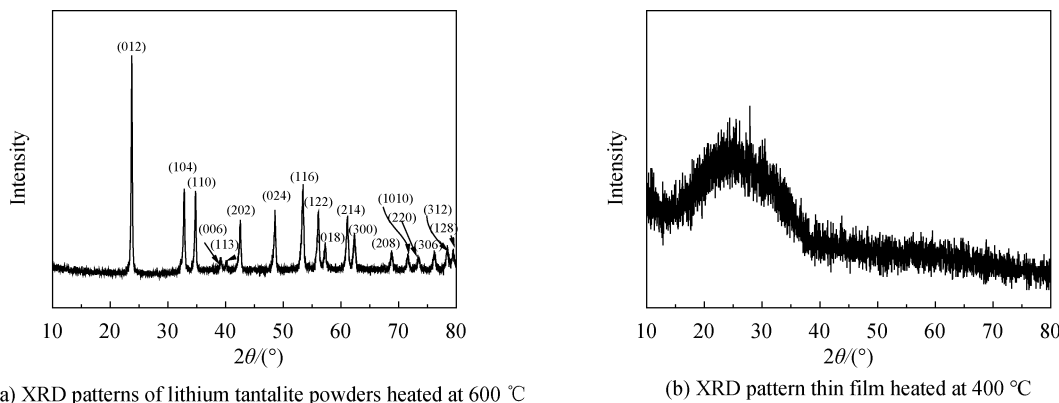


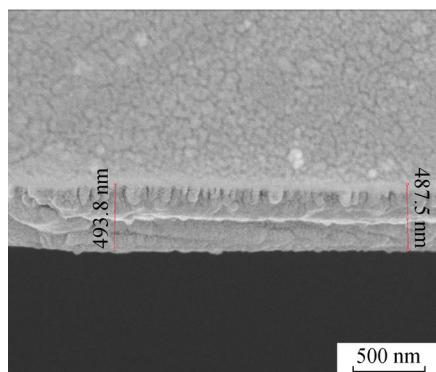
图1 600℃热处理的 LiTaO_3 粉末及旋涂后400℃热处理的薄膜的XRD谱

Fig. 1 XRD patterns of lithium tantalite powders heated at 600 °C and thin film heated at 400 °C

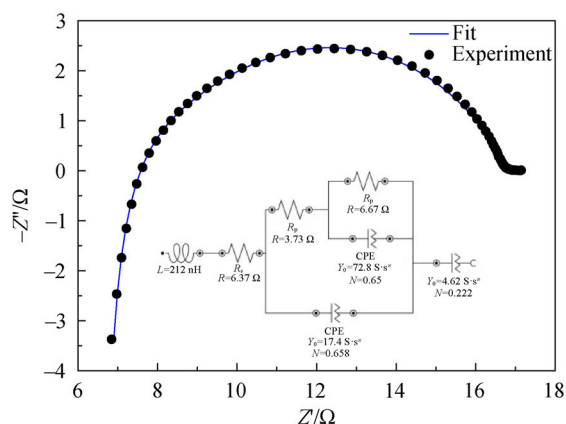
薄膜在 400 °C 热处理后的 XRD 谱如图 1b 所示, 薄膜为非晶态。

2.2 钽酸锂薄膜的电化学性能分析

在不锈钢基底上旋涂制备 500 nm 厚的钽酸锂薄膜, 其膜厚如图 2a 中 SEM 断面图所示, 通过磁控溅射在其表面沉积一层不锈钢电极, 制备出“不锈钢/钽酸锂/不锈钢”的结构, 并通过电化学工作站进行阻抗谱测试, 测试结果如图 2b 所示。其中溅射不锈钢电极面积为 4 cm²。对阻抗谱进行等效电路分析,



(a) Cross-sectional SEM image of LiTaO₃ film



(b) Electrochemical impedance spectroscopy and equivalent circuit fitting curve, inside is the equivalent circuit

图 2 旋涂钽酸锂薄膜的 SEM 断面照片和电化学阻抗谱及等效电路模拟结果

Fig. 2 Cross-sectional SEM image of LiTaO₃ film and electrochemical impedance spectroscopy and equivalent circuit fitting curve

2.3 基于液相法钽酸锂的电致变色器件性能分析

将在 NiO 薄膜上旋涂钽酸锂后制备得到的电致变色器件记为 EC-N, 在 WO₃ 薄膜上旋涂 LiTaO₃ 制备的电致变色器件标记为 EC-W。由于旋涂后的 LiTaO₃ 薄膜需要经过高温热处理, 对于电致变色器件 EC-N 意味着对其中的 NiO 膜层和底层 ITO 膜层进行了高温热处理, 其中 WO₃ 膜层为室温下制备; 对于标记为 EC-W 的器件, 其中的 WO₃ 膜层和底层 ITO 膜层经过了高温热处理, 而其中的 NiO 膜层和顶层的 ITO 膜层为室温条件下的膜层。

表 1 为 NiO、WO₃ 及 ITO 膜层的制备工艺参数。

表 1 NiO, WO₃ 和 ITO 薄膜的制备工艺参数

Table 1 Depositing parameters of NiO, WO₃ and ITO thin films

Target	Sputtering O ₂ and gas		Pressure /Pa	Power /W	Result film	Thickness /nm
Ni metal	O ₂ 、Ar	1:17	0.7	1000	NiO	300
W metal	O ₂ 、Ar	1:10	0.7	1000	WO ₃	300
ITO	O ₂ 、Ar	1:20	0.3	1200	ITO	600

其中模拟等效电路如图 2b 中所插入电路图所示, 得到阻抗 $R=16.8 \Omega$, 离子电导率通过式(1)计算:

$$\sigma = L/(R \cdot A) \quad (1)$$

式中: R 为阻抗; L 为薄膜厚度; A 为有效面积, 此处为溅射不锈钢电极面积 4 cm²; σ 为离子电导率。通过计算得到, 旋涂制备的钽酸锂薄膜室温离子电导率约为 $\sigma=7.44 \times 10^{-7} \text{ S/cm}$ 。

与磁控溅射制备的钽酸锂薄膜相比, 旋涂制备的薄膜具有相同数量级的离子电导率。

对于在 ITO 基底上制备的 NiO 和 WO₃ 薄膜 400 °C 热处理前后分别进行了 XRD 测试, 结果如图 3 所示。图 3a 为 NiO 薄膜的 XRD 谱, 在室温及 400 °C 热处理时均有结晶衍射峰, 其中标*号的为 ITO 衍射峰。对比 PDF 卡片 JCPDS 4-0835, 室温及 400 °C 热处理的 NiO 薄膜均为绿镍矿立方结构, 而热处理后不同衍射峰的强度有所变化, 这与文献报道一致^[46-47], 其中(111)峰强度相对变弱而(200)峰相对增强, 发生了(200)方向的择优取向。对于 WO₃ 薄膜, 如图 3b 所示, 在热处理前为非晶状态, 400 °C 热处理后出现强烈的衍射峰, 其中标星*号为 ITO 衍射峰。对比 PDF 卡片 JCPDS 43-1035, 400 °C 热处理后薄膜出现 WO₃ 单斜晶相, 且其中(200)峰衍射强度远强于其他峰强, 择优取向明显。如图中#号所示其中还出现化学组分为 WO_{3-x} 的物相。

图 4 是室温和 400 °C 热处理的 WO₃ 薄膜的 XPS 测试结果。如图 4a 所示, 相对于室温薄膜, 热处理后 W 的 4f_{7/2} 和 4f_{5/2} 均降低了 0.15 eV, 对 O 1s 能级对比也有相同的结果。O 1s 峰相对 W 4f 峰的强

度对比结果如图 4b 所示, 以 W 4f 峰的强度为 1, 室温和 400 °C 热处理的薄膜表面 O 1s 相对峰强分别为 1.098 和 1.152, 热处理后 O1s 峰强度明显增大。这表明热处理后表面氧原子数增加, 相应的室温薄膜表面相对具有较多的氧空位。Ottaviano 等^[48]与

Maffei 等^[49]的研究也分别独立得出相同的结果, 他们对此的解释是在真空热处理时 WO_3 薄膜中的氧会从内部往表面迁移。因此此处在旋涂了离子导体层后进行热处理时在 WO_3 膜层中同时形成了结晶相和内部的缺氧相, 即 WO_{3-x} 相。

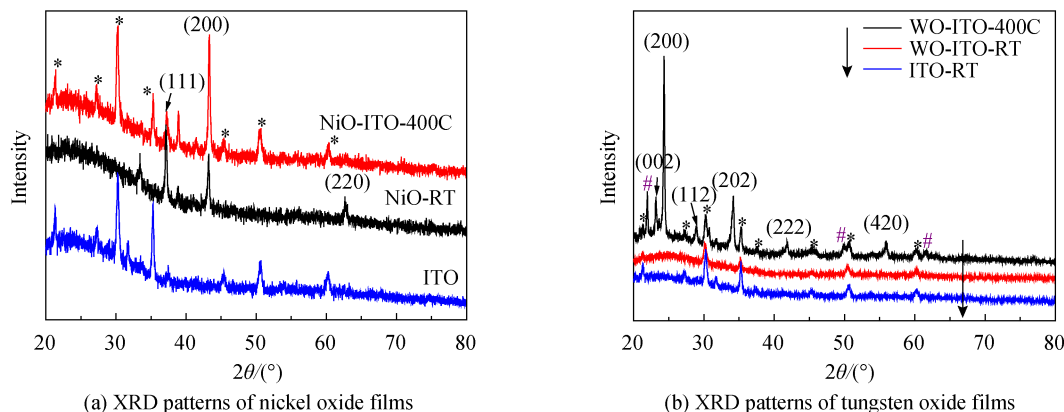


图 3 ITO 基底 NiO 和 WO_3 在 400 °C 热处理前后的 XRD 谱

Fig. 3 XRD patterns of nickel oxide films and tungsten oxide films on ITO before and after 400 °C

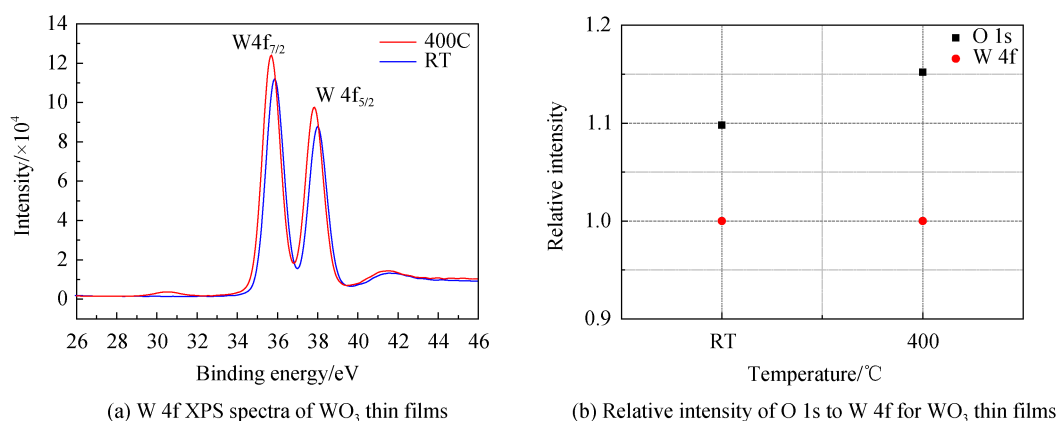


图 4 室温及 400 °C 热处理后 WO_3 薄膜的 XPS 图谱和室温与 400 °C 热处理后 O 1s 能谱相对 W 4f 能谱强度的变化

Fig. 4 W 4f XPS spectra of WO_3 thin films and the relative intensity of O 1s to W 4f for WO_3 thin films at RT and 400 °C

对于 ITO 薄膜热处理前后的 XRD 谱分析表明 400 °C 热处理前后没有出现明显的物相和晶体的变化。热处理后 ITO 薄膜的方阻变大, 由室温下 $10 \Omega/\square$ 增大到约 $30 \Omega/\square$ 。

图 5 为不同基底上旋涂的 LiTaO_3 薄膜表面形貌及粗糙度测试结果, 其中的 LiTaO_3 薄膜由一些细小的颗粒组成, 表面较为平整, 以 WO_3 薄膜为基底制备的 LiTaO_3 薄膜具有较大的粗糙度, 约为 2.36 nm。在 ITO/NiO 表面上旋涂制备的 LiTaO_3 薄膜粗糙度较小, 约为 1 nm。这可能与热处理前后 NiO 薄膜的结晶性能变化较小, 而 WO_3 由非晶转变成结晶性能更好的膜层有关。

2.3.1 器件 EC-N 的性能与分析 通过电化学工

作站对器件进行不同偏压下的计时电流扫描, 并在紫外-可见-近红外分光光度计中实时记录其对 550 nm 波长可见光的透过率变化曲线, 结果如图 6a 所示。随着扫描电压的增加, 着色态透过率逐渐降低, 而褪色态的可见光透过率略有增加。器件着色态透过率、褪色态透过率及可见光调节幅度随外加电压的变化曲线如图 6b 所示, 其中器件的着色态可见光透过率随电压增加变化显著降低, 可见光透过率的调节幅度显著增大。而褪色态透过率虽然也略有增加, 但是变化幅度很小。当外加电压为 5 V 时, 透过率调节幅度最大达到 26%, 此时器件的着色时间和褪色时间分别为 50 s 和 56 s。器件需要较高的电压才能实现比较大幅度的透过率变化可能与液相离子导

体层具有一定的电子导电性有关, 可以通过合理的工艺降低其电子导电性, 从而降低其转变电压。

图 7a 是器件 EC-N 的初始态、着色态与褪色态的透过率曲线。其中着色态为施加 -4 V 外加电压后器件的透过率曲线, 可以看到, 器件着色态能显著降低可见光的透过率。褪色态为施加 2 V 反向电压

后器件的状态, 从图中可以看出其透过率比初始态略有增加。对器件进行循环扫描, 结果如图 7b 所示, 在循环 60 次后器件的褪色态和着色态透过率基本保持不变, 性能保持稳定, 没有明显的衰减。可见基于液相法离子导体层制备的电致变色器件可以具有很好的循环稳定性。

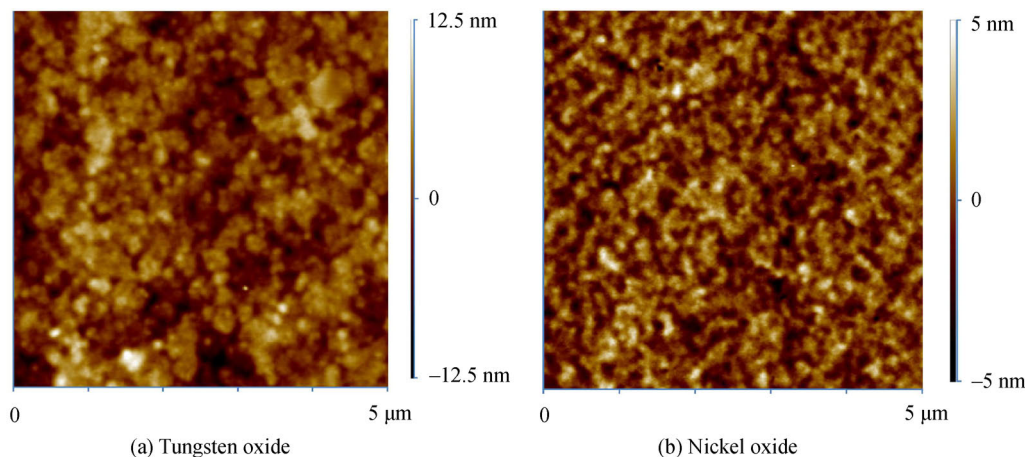


图 5 WO_3 基底和 NiO 基底上 LiTaO_3 薄膜热处理后的 AFM 形貌

Fig. 5 AFM images of lithium tantalite on tungsten oxide and nickel oxide film after heat treatment

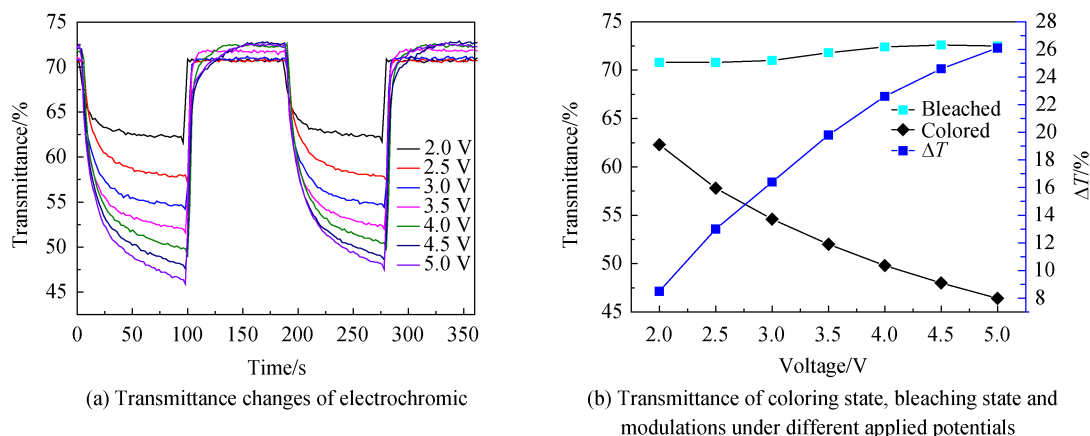


图 6 电致变色器件 EC-N 透过率变化曲线以及着色态透过率、褪色态透过率和可见光调节幅度随外加偏压的变化

Fig. 6 Transmittance changes of electrochromic devices EC-N and transmittance of coloring state, bleaching state and modulations under different applied potentials

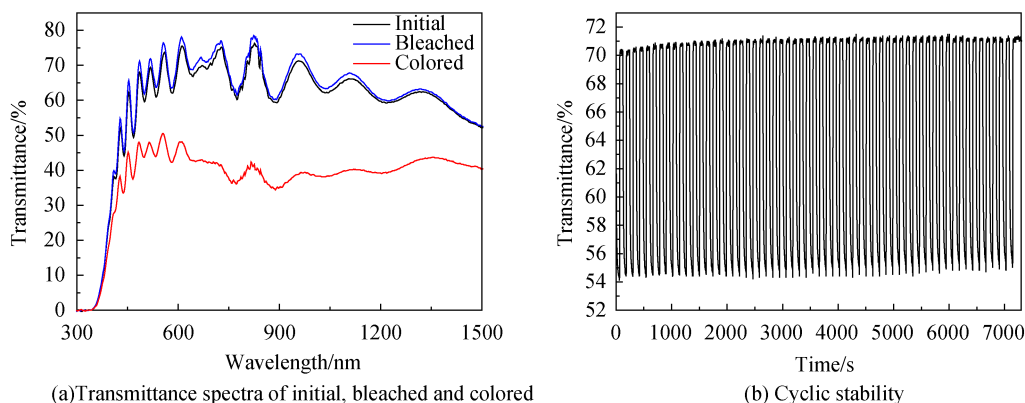


图 7 器件 EC-N 的初始态、着色态与褪色态的透过率图谱和循环稳定性

Fig. 7 Transmittance spectra of initial, colored and bleached state and cyclic stability of EC-N

2.3.2 器件 EC-W 的性能与分析 对电致变色器件 EC-W 在计时电流扫描下进行透过率随时间变化的测试, 其结果如图 8a 所示。外加电压较低时比如在 2.0 V 和 2.5 V, 透过率变化很小, 随着电压继续增大, 透过率变化明显变大。如图 8b 为电致变色器件 EC-W 在不同外加电压下透过率变化的数值, 在施加 2.0 V 和 2.5 V 外加电压时, 透过率调节幅度均小于 5%, 电压增加为 3 V 时, 透过率变化率快速增大至 14% 左右, 然而此时着色和褪色所需的时间也快速增加, 着色和褪色速率降低, 其中 3 V 时的褪色时间大于扫描电压所设定的时间 120 s。如图 9a 为电致变色器件 EC-W 初始态、着色态和褪色态的透过率曲线, 其中着色态对近红外波段透过率调节效果明显。图 9b 为其多次循环时透过率变化及循环稳定性。从图 9 中可以看出, 随着循环次数的增加褪色态的透过率降低, 而着色态的透过率不断升高, 器件性能出现衰减。

对比 EC-N 与 EC-W 器件的性能可知, 以 NiO 薄膜为基底旋涂 LiTaO₃ 离子导体层制备的电致变

色器件具有更好的可见光调节性能及更好的循环稳定性, 而且转变速率更快。图 10a 中对比了器件 EC-N 与 EC-W 褪色态的褪色时间随外加电压的变化, 器件 EC-N 的褪色速率随着外加电压的增加会有所减慢, 然而褪色时间均在 1 min 以内。NiO 热处理对器件的性能影响较小且会使器件性能减弱^[46–47], 因此可以认为 2 组器件的性能差距主要是由 WO₃ 膜层的变化引起的。

对于器件 EC-W, 在提高外加电压时, 伴随透过率调节幅度的提高, 电致变色转变发生所需的时间急剧增加, 这可能由于晶态 WO₃ 薄膜的 Li⁺ 的插入和抽出更难, 需要更高的激活能有关。对比二者在着色态时可见近红外波段的透过率曲线, 如图 10b 所示, 器件 EC-W 对近红外波段的透过率调节效果更加明显。对于金属氧化物的近红外波段的调控, 普遍认为是由于其中的局域表面等离子激元共振 (Localized surface plasmon resonance, LSPR) 引起的, 对于缺氧的 WO_{3-x} 的电致变色性能的研究展示了其可见和近红外双波段调控的特性^[50–52], WO_{3-x} 表面

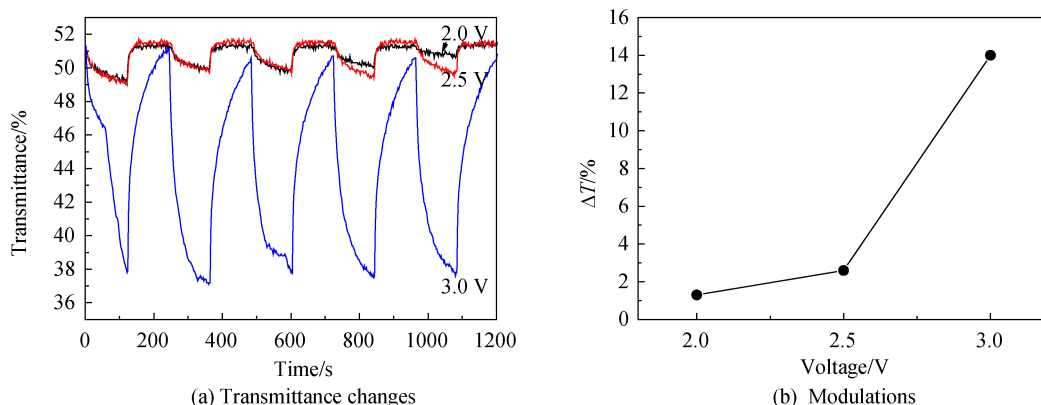


图 8 电致变色器件 EC-W 不同外加电压下的透过率转变曲线及可见光透过率调节幅度

Fig. 8 Transmittance changes of EC-W at under different applied potentials and its visible light transmittance modulations

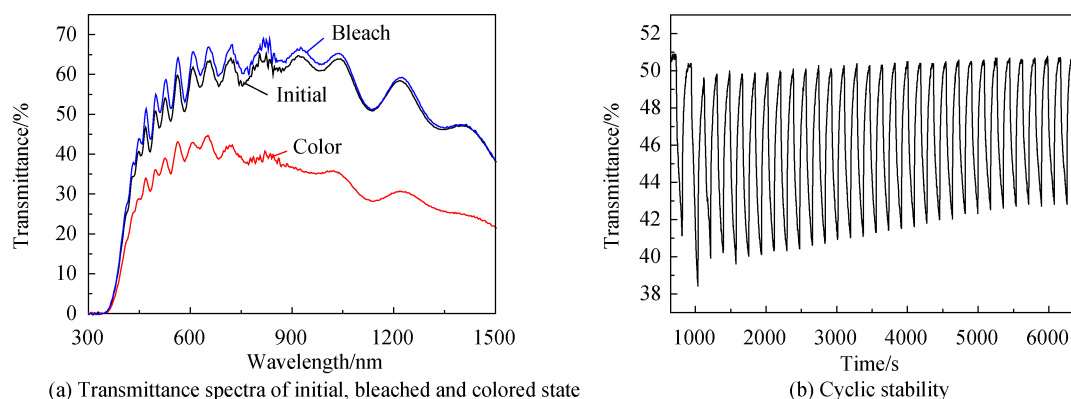


图 9 电致变色器件 EC-W 初始态、着色态和褪色态的透过率曲线以及循环稳定性

Fig. 9 Transmittance spectra of initial, colored and bleached state and cyclic stability of EC-W

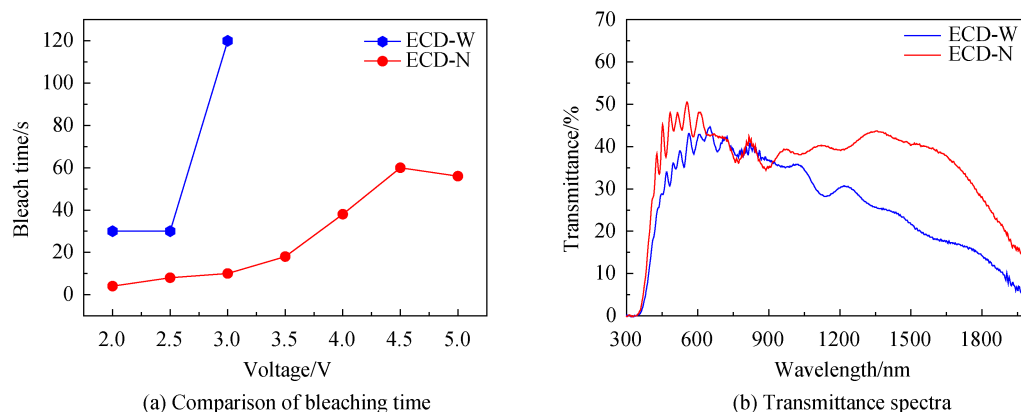


图 10 电致变色器件 EC-N 与 EC-W 的褪色时间的对比曲线与着色态透过率曲线
Fig. 10 Comparison of bleaching time and transmittance spectra of colored state of EC-N and EC-W

的 Li^+ 吸附脱附引起 LSPR 效应, 进而产生对近红外 (NIR) 的动态调控。对于器件 EC-W, 由于热处理时其中的非晶氧化钨膜层夹在 ITO 和 LiTaO_3 膜层之间, 相当于接近无氧的环境, 热处理后使得一部分薄膜形成化学计量比 WO_3 结晶相, 而另一部分由于氧缺失形成缺氧的 WO_{3-x} 相, 进而由于缺氧相在 Li^+ 插入和抽出的 LSPR 效应增强了对近红外波段的调控。这一现象为可见近红外双波段调控的电致变色器件的制备提供了一种可行方案, 即通过调节热处理的温度和时间, 控制其中的结晶态与缺氧组分比例, 在不显著影响其转变速率的情况下提高对近红外波段的调控性能, 从而实现光和热的双调控。

3 结论

1) 以 NiO 为基底旋涂离子导体层制备的电致变色器件 EC-N 具有较快的着色和褪色转变速率, 通过提高对器件施加的工作电压, 可以显著提高器件对可见光透过率调节的幅度, 同时提高电压也会增加器件着色和褪色时间。当外加电压为 5 V 时, 最高调节幅度为 26%, 不同外加电压下其转变时间均在 1 min 之内。且器件在多次循环之后透过率调节幅度没有明显衰减, 器件性能保持稳定。

2) 以 WO_3 为基底旋涂离子导体层制备的电致变色器件 EC-W 在施加低于 3 V 电压时器件透过率调节幅度较低, 小于 5%, 当增加电压到 3 V 时, 调节幅度快速增加, 但是器件的着色与褪色的转变速率也急速下降, 其着色褪色时间超过所设定的 120 s。这可能与热处理后 WO_3 膜层的结晶态形成有关, 结晶的形成阻碍了离子的插入和抽出过程。

3) WO_3 膜层的热处理可以提高器件 EC-W 对近红外波段透过率的调节性能, 根据这一现象可以通过对 WO_3 膜层进行适当的热处理来实现器件对可

见光和近红外波段的双波段调控。

(第二十七届中国科协年会学术论文)

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Electrochromic Devices with Ion Conductor Layers Prepared by Sol-gel Method and Their Performances

SU Wenjing^{1,2}, WANG Tianqi^{1,2}, JIN Kewu^{1,2}, TANG Yongkang^{1,2}, SHEN Hongxue^{1,2}, LI Gang^{1,2}

(1. State Key Laboratory of Advanced Glass Materials, CNBM Research Institute for Advanced Glass Materials Group Co., Ltd., Bengbu 233018, Anhui, China;

2. Silica-based Materials Laboratory of Anhui Province, Bengbu 233018, Anhui, China)

Extended Abstract

Introduction Electrochromic device (ECD) is comprised of five superimposed layers, *i.e.*, transparent conducting layer, electrochromic layer, ion conductor layer, ion storage layer and another transparent conducting layer, respectively. It can modulate the amount of solar radiation transmitting through it under applied voltage, often used as smart windows or facades to adjust the light and heat entering buildings proactively, which can sufficiently reduce the energy consumption. The existing ECDs are mainly fabricated by a magnetron sputtering method, which has a low productivity and high cost, especially for the ion conductor layer. Sol-gel method is a simple and relatively cheap method for preparing thin films, and massive researches are conducted on sol-gel electrochromic thin films such as tungsten oxide, nickel oxide *etc.*. In this work, an ion conductor layer was prepared by a sol-gel method, and its application in electrochromic device and their performance were also investigated.

Methods Lithium tantalite sol was synthesized with lithium acetate (LiAc) and tantalum pentaethoxide (TaEt) as precursors and 1,2-Propanediol as a solvent. The molar ratio of LiAc and TaEt was 1:1. Lithium tantalite thin films were prepared by a spin coating method and heat-treated in air at 400 °C for 2 h. Some of the sol was dried and the subsequently formed powder was heated at 600–700 °C. The phase compositions of the films and powders were characterized by X-ray diffraction (XRD), and the electrochemical properties of thin films were analyzed.

The electrochromic devices with a structure of ITO/NiO/LiTaO₃/WO₃/ITO were prepared by PVD method and subsequent sol-gel method. The tungsten oxide or nickel oxide thin film layer was firstly sputtered on the ITO glass and then lithium tantalite thin films were spin-coated onto the as prepared films. After heating process at 400 °C for 2 h, another layer of the tungsten oxide or nickel oxide films were sputtered, and another layer of ITO thin film was finally sputtered as a conducting electrode. The electrochromic devices were noted as EC-N when lithium tantalite was spin-coated onto nickel oxide films and as EC-W when lithium tantalite was spin-coated onto tungsten oxide films. The transmittance changes were measured by UV-vis-IR spectrometer.

Results and discussion The XRD patterns show that powders dried and heated from the sol are a polycrystalline lithium tantalite, and thin films are amorphous. The analysis of electrochemical impedance spectroscopy indicates that the sol-gel lithium tantalite thin film has an ionic conductivity of 7.44×10^{-7} S/cm at room temperature, which is comparable to that of sputtered film. As for the devices, the XRD patterns show that nickel oxide thin film layers are both polycrystalline in EC-N and EC-W, while tungsten oxides is polycrystalline in EC-W and amorphous in EC-N. The XRD patterns and XPS spectra also show the existence of WO_{3-x} phase in polycrystalline tungsten oxide films.

For electrochromic properties of the two groups of devices, transmittance regulations are measured at a fixed wavelength of 550 nm. For both groups, the differences of transmittance between colored and bleached state increase with increasing voltage. The maximum of transmittance change for EC-N is 26% at 5 V, with transmittance of around 72% at bleached state and 46% at colored state. Its coloring time is 50 s and bleaching time is 56 s. The results of cyclic test show that the differences of colored and bleached states keep stable, no obvious degeneration occurs after 60 cycles. The transmittance changes for EC-W have a lower value when applied the same voltages as in EC-N, and the switching speed is much slower. Its transmittance change is 14% at 3 V, while the coloring and bleaching time are both larger than 2 min, exceeding the setting range. It can be concluded that EC-N has a better property for regulation of visible light, and crystallinity can slow the switching process.

The transmittance spectra of colored states in vis-NIR range show that EC-W has a significant modulating performance for NIR, which can be attributed to the existence of WO_{3-x} components. As reported, oxygen deficient components can generate a local surface plasmon resonance effect that can result in absorption in the spectral range of NIR.

Conclusions Electrochromic devices fabricated by a process that lithium tantalite was spin-coated on nickel oxide had better electrochromic properties in a visible spectral range, with larger optical modulations and a higher switching speed less than 1 min. The devices with lithium tantalite spin-coated on the tungsten oxide films could have a slower coloring and bleaching rate, while showing a better near-infrared modulation effect. These results indicated a routine for the realization of electrochromic devices that could modulate light and heat simultaneously and independently.

Keywords sol-gel method; lithium ion conductor layer; electrochromism; all solid state inorganic electrochromic device; localized surface plasmon resonance; near-infrared modulation