中国科学技术大学
University of Science and Technology of China

NiO/ WO3 based Electrochromic films

电致变色玻璃

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Contents

目录

1 Research background

2 Experimental principle

3 Experiment content

4 Data processing

5 Summary

1. Electrochromic phenomenon

Electrochromism refers to the reversible discoloration of materials under the action of redox reaction under the condition of voltage or current.

According to the mechanism, it can be divided into three types: ions enter the material through the electrolyte to cause discoloration; The metal film is electrodeposited on the observation electrode; Colored insoluble organic matter precipitated on the observation electrode.

At present, electrochromic materials are mainly used as window making materials for buildings or vehicles, such as automobile rearview mirror, airplane porthole, etc. In the future, electrochromism will also have a strong application prospect in military, aerospace, medical and health, nuclear reactor protection intelligent robots and other fields, such as infrared transmitters used to make dynamic changes (such as fast switching response, automatic intelligent control).

2. Electrochromic material

分类	材料		颜色转换
无机电致变色材料	过渡金属氧化物	WO_3	深蓝色/透明
		MoO_3	深蓝色/透明
		Nb_2O_5	浅蓝色/透明
		TiO_2	浅蓝色/透明
		NiO	透明/黑色
		IrO_2	透明/蓝黑色
		CoO_x	绿色/红色
	络合物	PB	白/蓝/绿色
	贵金属	Ag	透明/镜面/多色
有机电致变色材料	导电聚合物	PANI	黄/绿/蓝色
		PEDOT	透明/蓝色
	有机小分子	紫罗精	透明/深绿色

Contents

目录

1 Research background

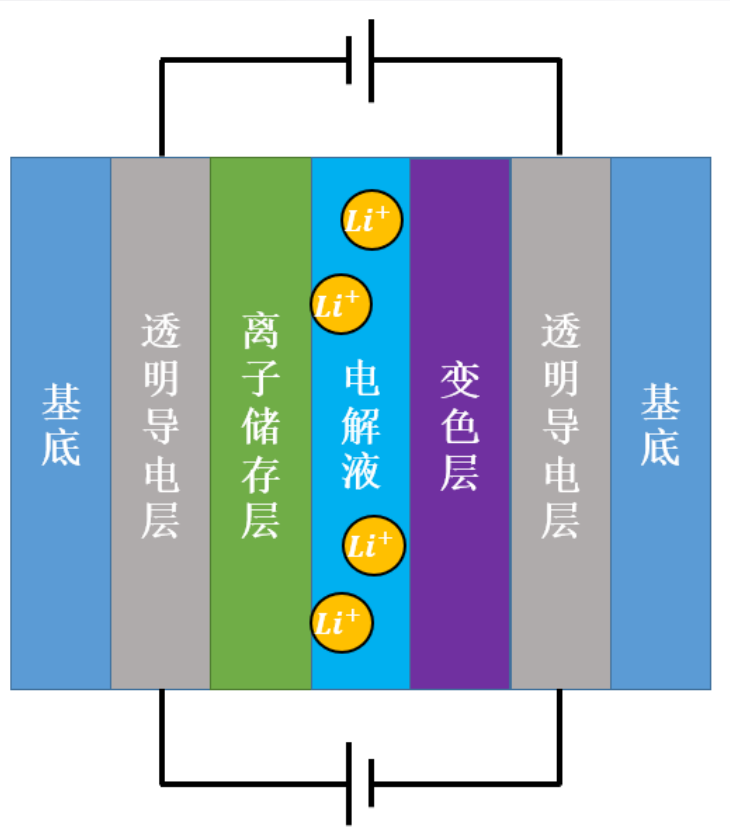
2 Experimental principle

3 Experiment content

4 Data processing

5 Summary

1. Electrochromic mechanism



$$WO_3 + x\,M^+ + x\,e^- \leftrightarrow M_x\,WO_3$$

$$\mathrm{NiO}(\text{漂白态}) + \mathrm{OH}^- \leftrightarrow \mathrm{NiOOH}(\text{着色态}) + e^-$$

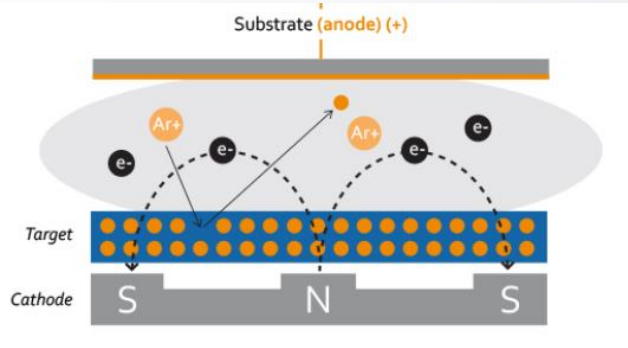
$$\mathrm{Ni(OH)_2}(\text{漂白态}) \leftrightarrow \mathrm{NiOOH}(\text{着色态}) + \mathrm{H}^+ + e^-$$

$$\mathrm{NiO_x}(\text{初始沉积态}) + \mathrm{yM}^+ + \mathrm{ye}^- \leftrightarrow \mathrm{M_yNiO_x}(\text{漂白态})$$

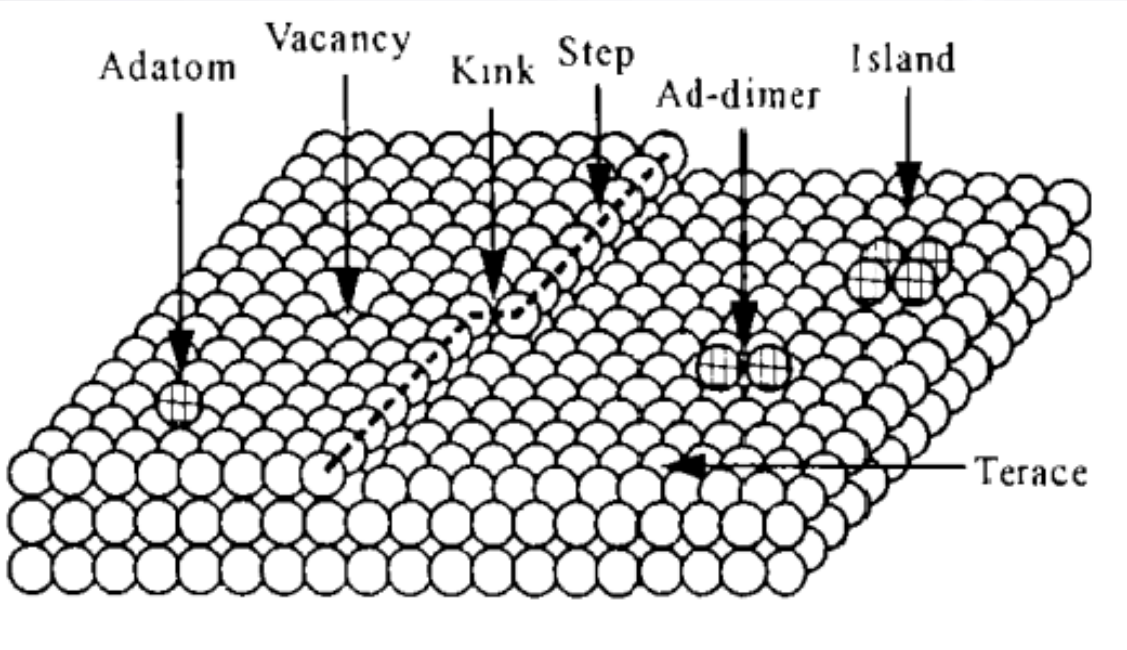
$$\mathrm{M_yNiO_x}(\text{漂白态}) \leftrightarrow \mathrm{M_{y-z}NiO_x}(\text{着色态}) + \mathrm{zM}^+ + \mathrm{ze}^-$$

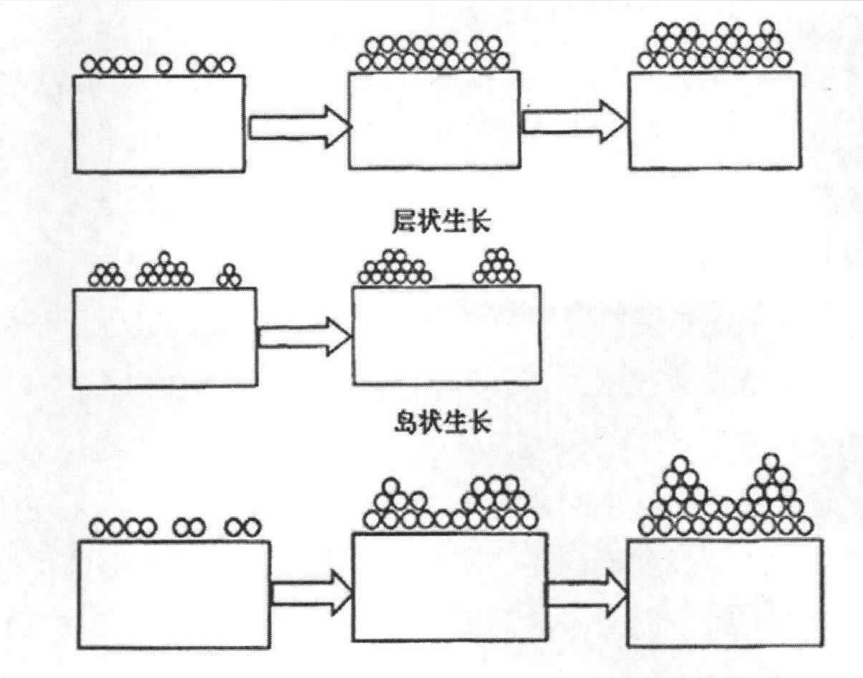
2. Magnetron sputtering coating

Place the target on the cathode and fill the vacuum coating chamber with process gas. The process gas is a mixture of argon (Ar) and oxygen in a certain proportion; After that, high voltage is applied to the two sections to make them glow discharge. At this time, Ar is ionized, producing positive Ar ions and new electrons; New electrons fly to the substrate, and Ar ions accelerate to fly to the cathode target under the action of electric field, and bombard the target surface with high energy to make the target sputter.



3. Micro mechanism of thin film growth





The motion of film atoms on the substrate surface can be simplified into three dynamic processes: deposition process, diffusion process and desorption process.
(In the absence of surfactant mediation) The increase of temperature and the decrease of deposition rate will lead to the easier diffusion of adsorbed atoms to vacancies, and the film tends to grow in layers with complete and compact structure. On the contrary, the internal structure of the membrane is more loose.

Contents

目录

1 Research background

2 Experimental principle

3 Experiment content

4 Data processing

5 Summary

Research Background
Experimental Principle
Experiment Content
Data Processing
Summary

1. Coating

I. The surface of the coating substrate including ITO glass and silicon wafer was cleaned by ultrasonic cleaning instrument and plasma cleaning instrument.

II. Fix ITO glass and silicon chip on the corresponding position of the substrate of the magnetron sputtering instrument

III. Install the corresponding target (tungsten target or nickel target)

IV. Vacuum magnetron sputtering coating under different experimental variables

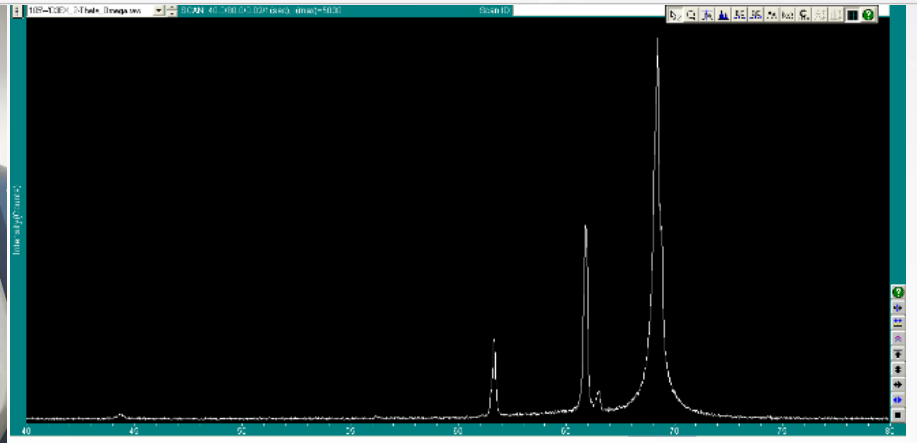
Research Background
Experimental Principle
Experiment Content
Data Processing
Summary

Sputtering conditions of 9 films

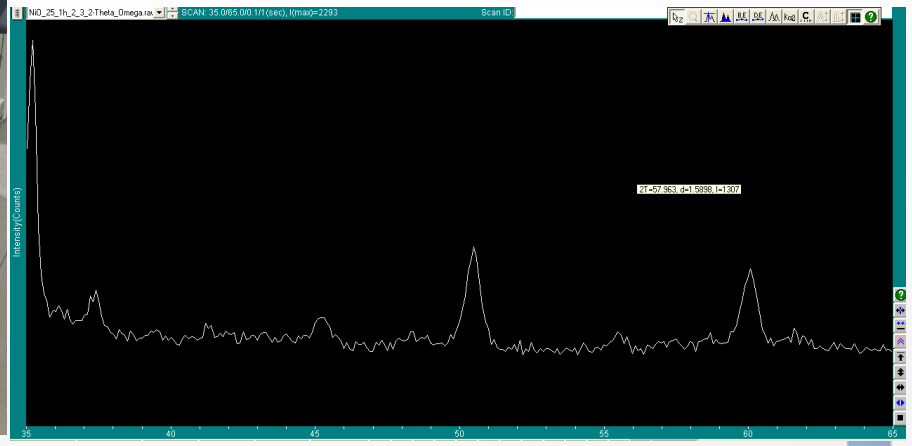
Chromotropic substance	Sputter temperature (℃)	Ar:O2 (sccm)	Sputtering power (W)	Sputtering time (h)
WO3	25	15:15	150	1
WO3	25	15:15	100	2
WO3	200	10:20	100	1
WO3	200	15:15	100	1.5
WO3	200	15:15	100	1
WO3	200	15:15	100	0.5
NiO	200	15:15	100	1
NiO	200	10:20	100	1
NiO	25	10:20	100	1

2. Structural characterization （XRD）

Research Background
Experimental Principle
Experiment Content
Data Processing
Summary



WO3

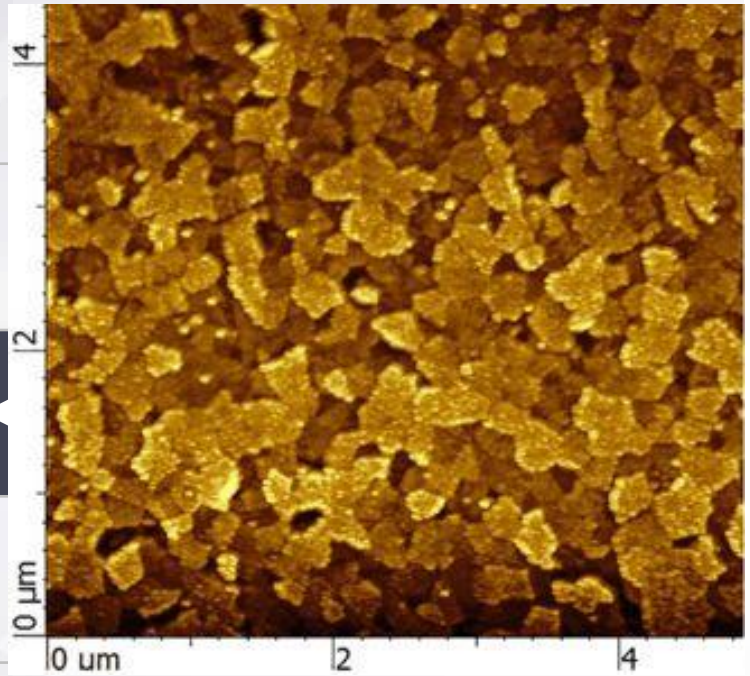


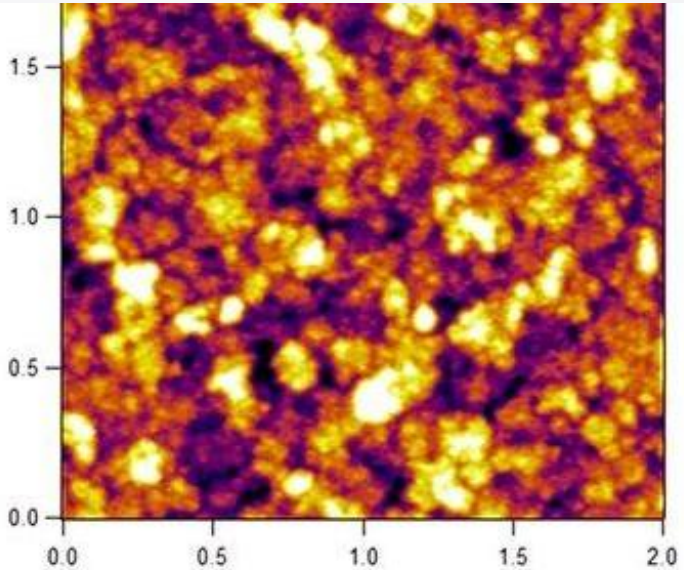
NiO

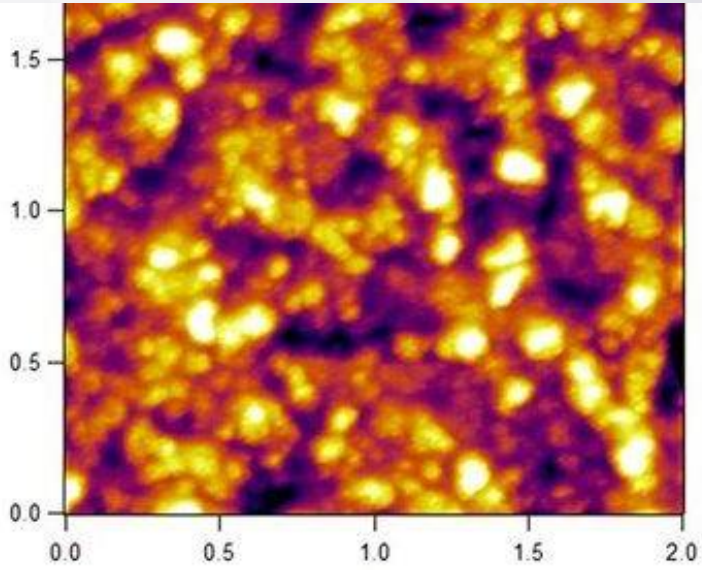
Filter out the diffraction peaks of silicon wafer, and the rest are the diffraction peaks of amorphous WO3 and NiO

3. Morphology characterization （AFM）

Research Background
Experimental Principle
Experiment Content
Data Processing
Summary





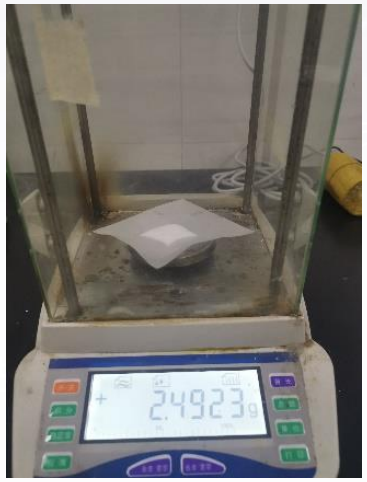


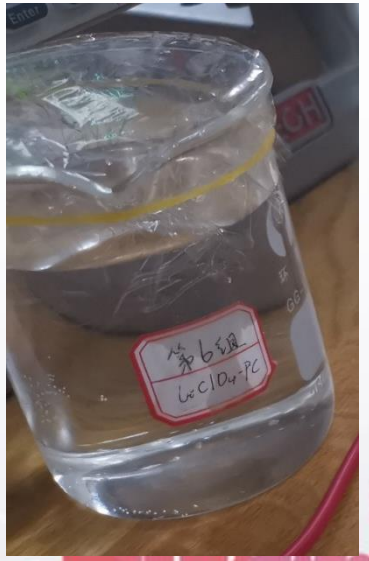
实践难点

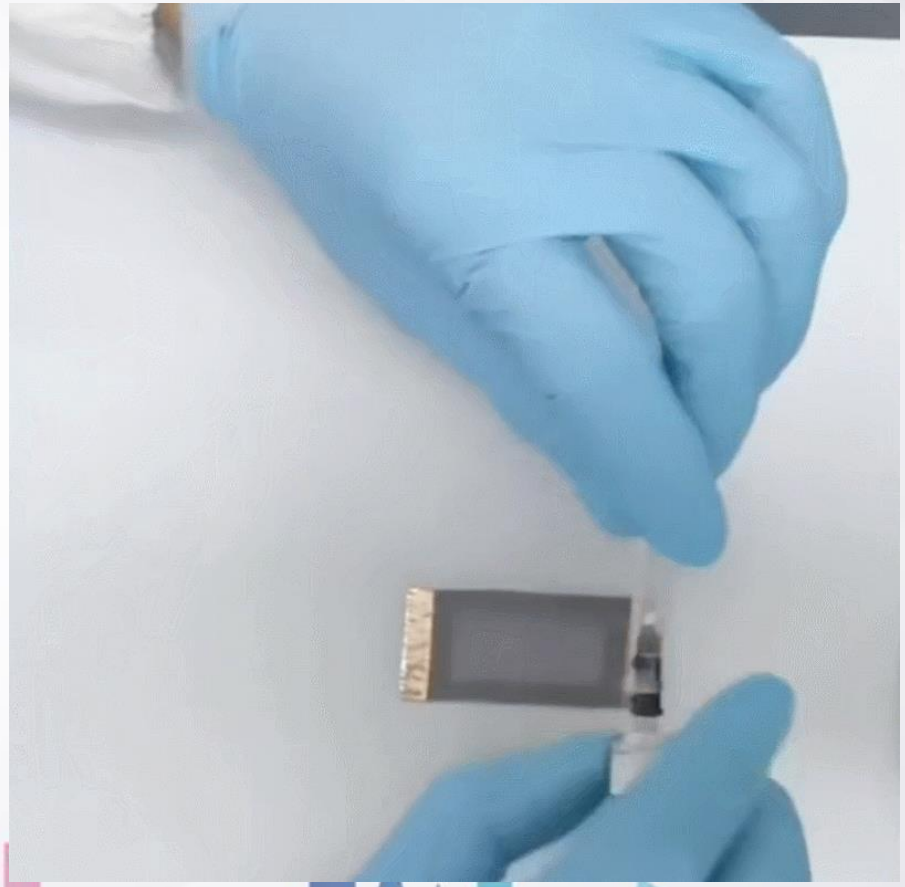
Tungsten oxide and nickel oxide films are amorphous, WO3 at 25 ℃ is rougher than that at 200 ℃

4. Liquid electrolyte （1mol/L LiClO4/PC）

Research Background
Experimental Principle
Experiment Content
Data Processing
Summary

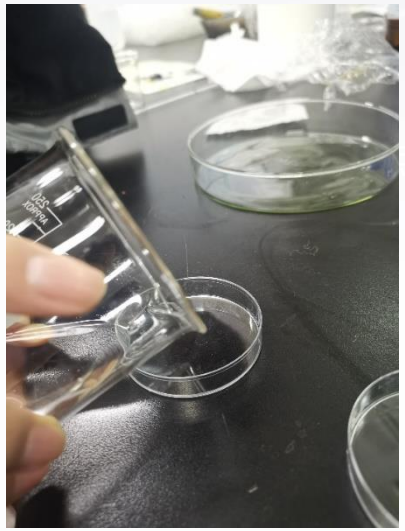


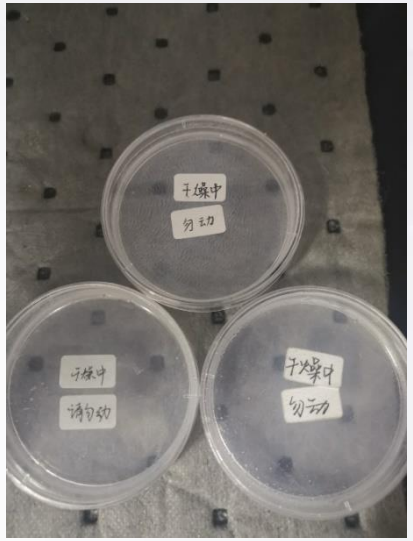


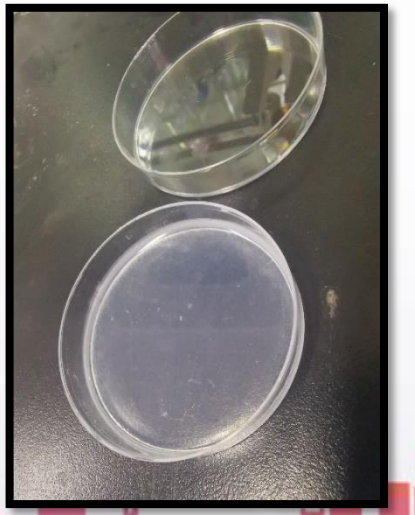


5. Solid electrolyte （LiClO4/PC+PMMA+ Tetrahydrofuran ）

Research Background
Experimental Principle
Experiment Content
Data Processing
Summary

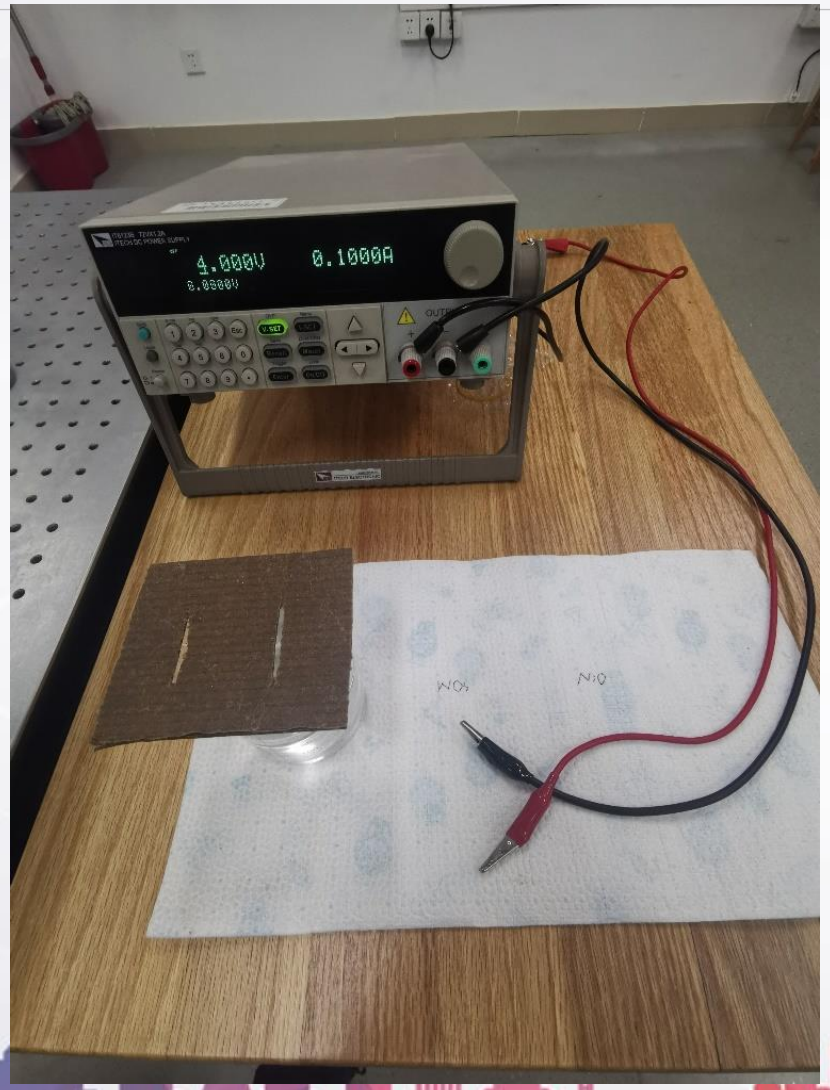


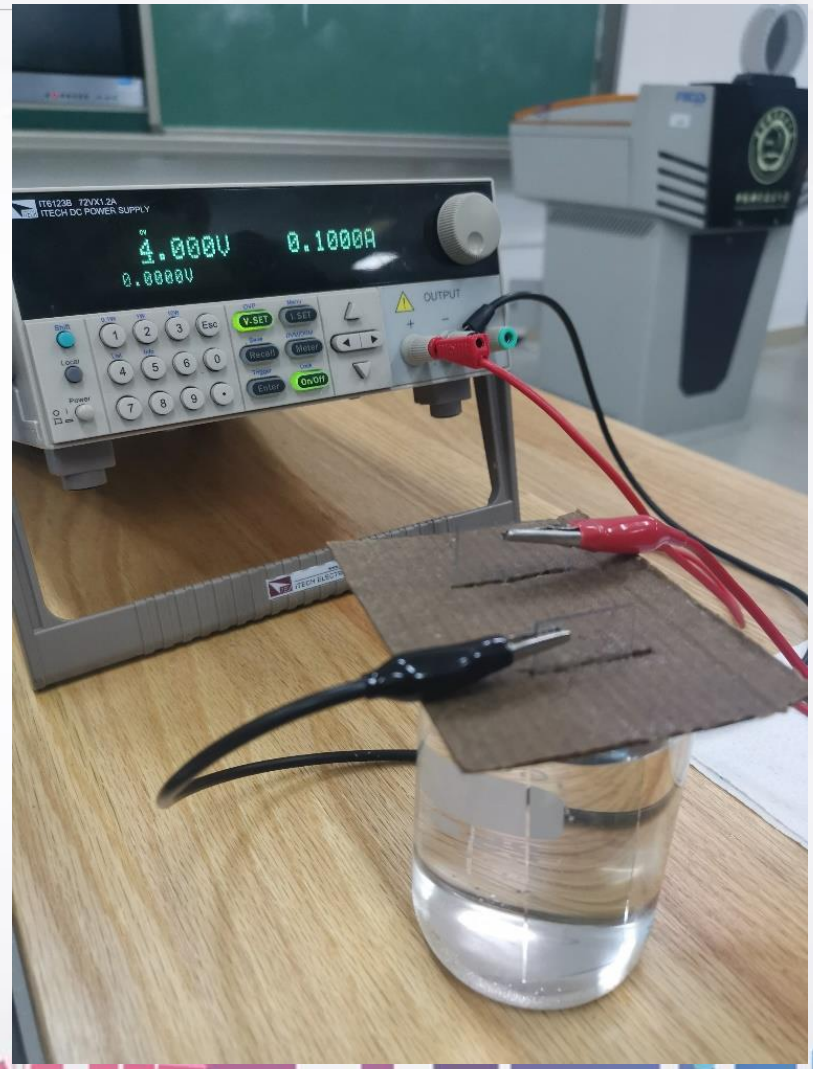




Research Background
Experimental Principle
Experiment Content
Data Processing
Summary

1. Device for discoloration

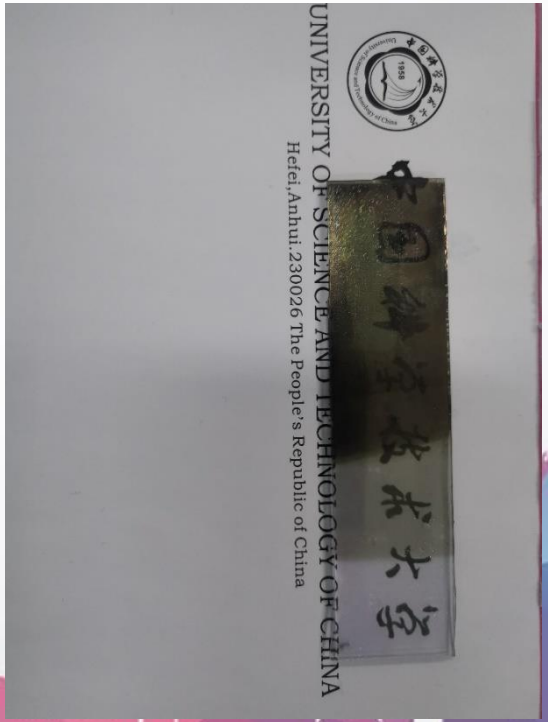




Research Background
Experimental Principle
Experiment Content
Data Processing
Summary

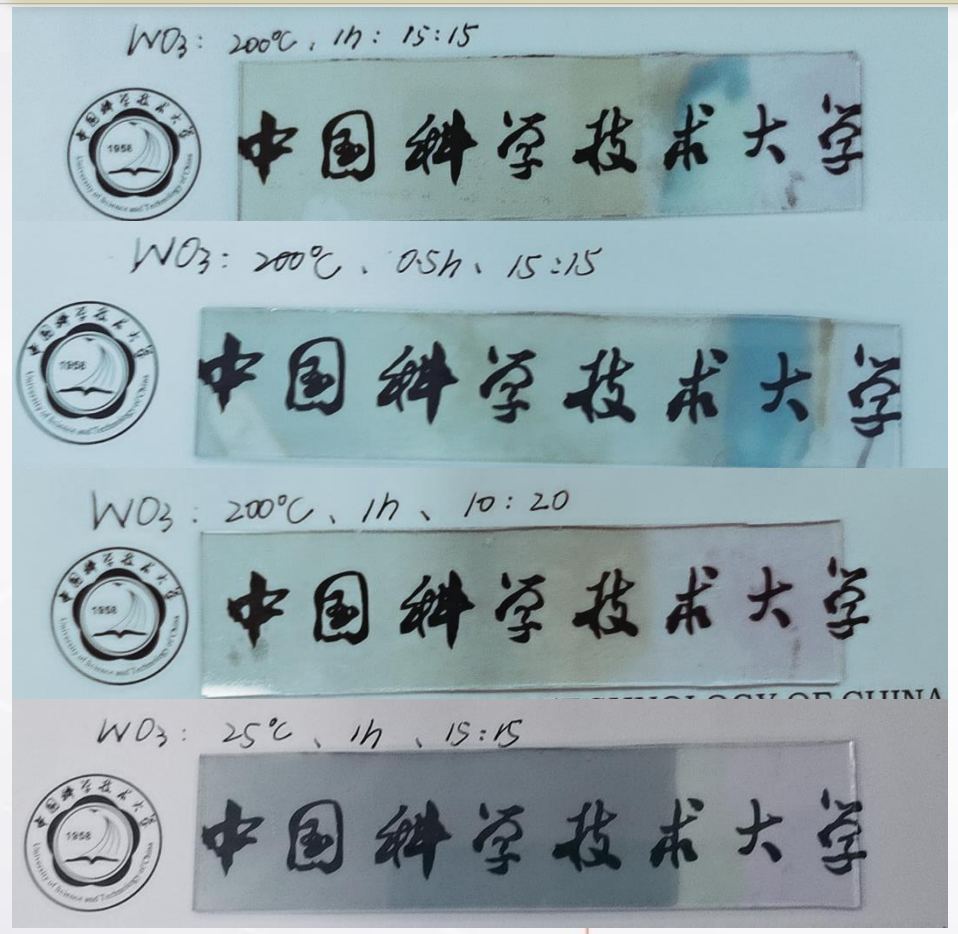
2. Selection of voltage

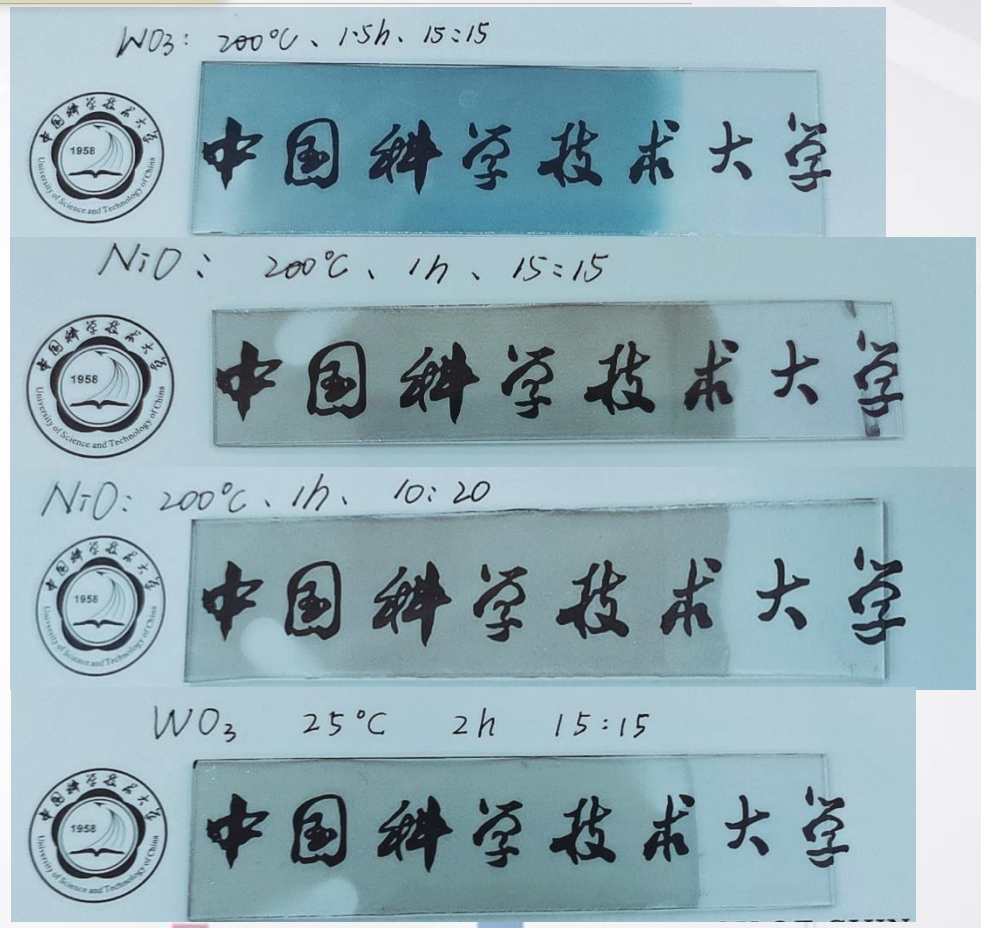
Through our test, it is found that if the voltage is 4.5V or above, the ITO layer will turn yellow (irreversible under high voltage) when it is reduced at the cathode, which interferes with the experimental phenomenon; When the voltage is too low, the discoloration time is too long. So we uniformly take the discoloration voltage as 4.000V, and the power on time is 1min each time.



3. Discoloration effect display

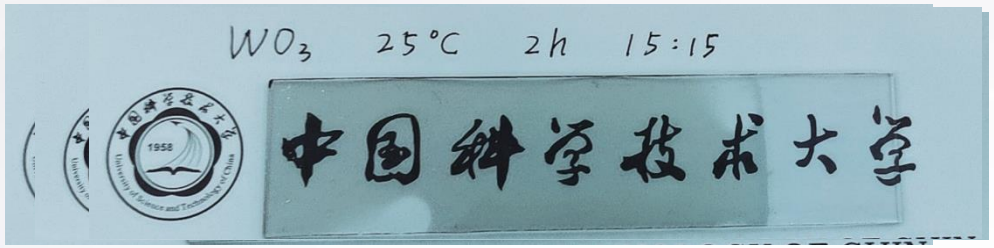
Research Background
Experimental Principle
Experiment Content
Data Processing
Summary

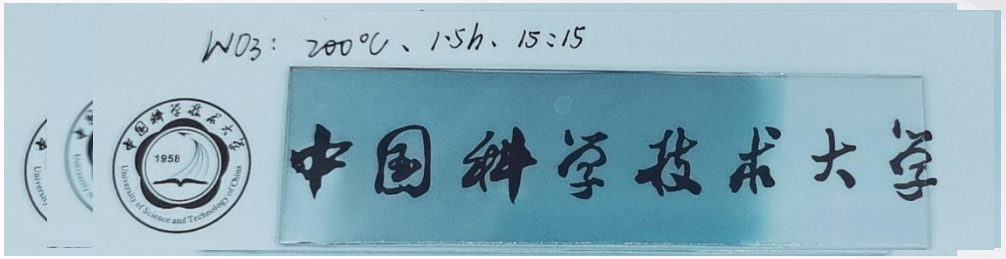


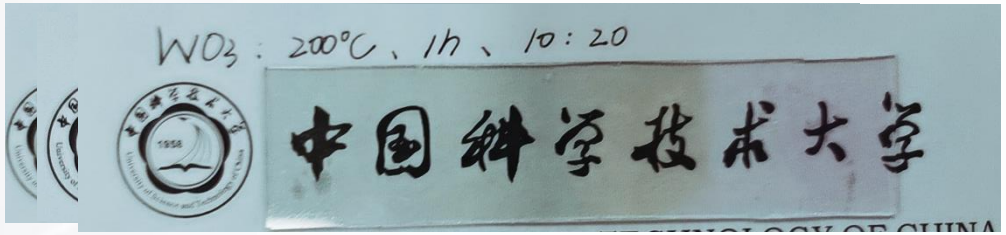


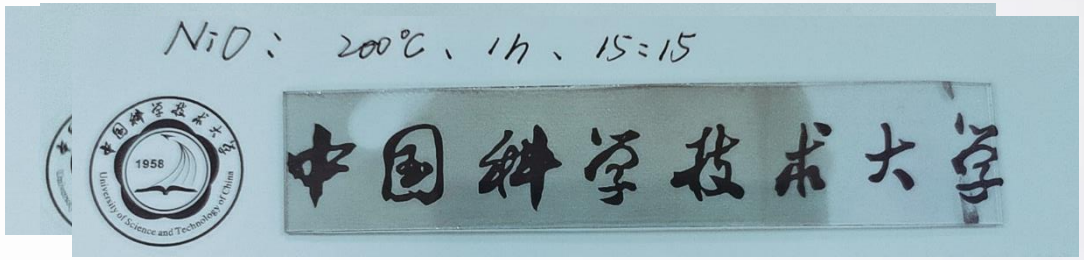
4. Circulation effect display

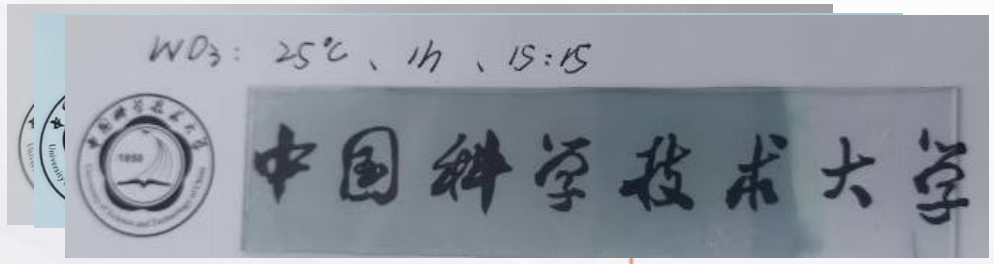
Research Background
Experimental Principle
Experiment Content
Data Processing
Summary

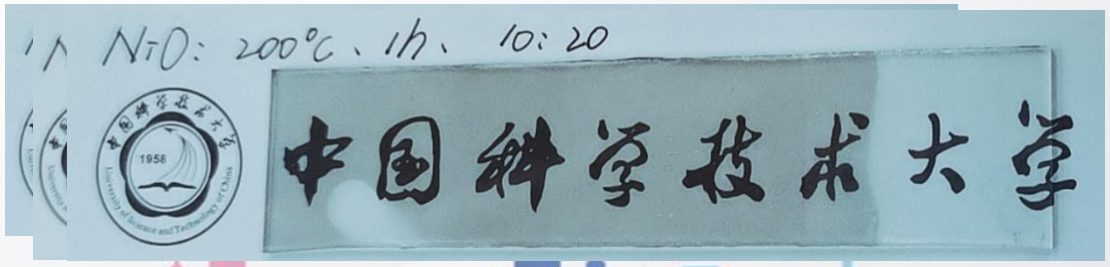








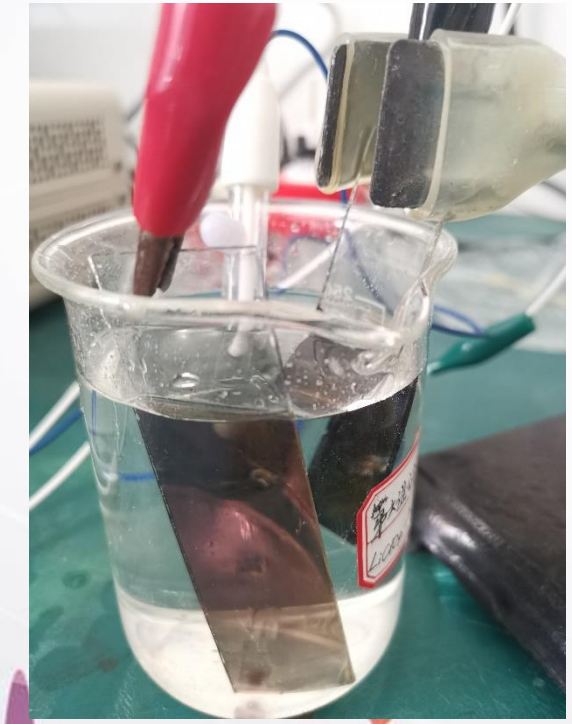




Research Background
Experimental Principle
Experiment Content
Data Processing
Summary

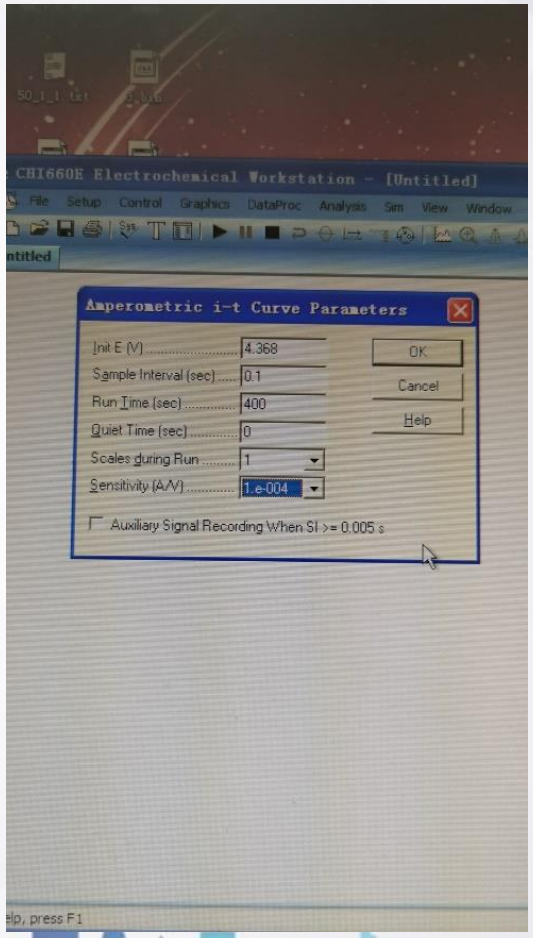
4. Failed 25℃ NiO

After coloring, it looks like a mirror. When it fades, the cathode ITO turns black quickly. There is sediment at the bottom of LiClO4/PC solution. There are [N] (2+) ions left in LiClO4/PC. We guess that Ni is not oxidized when coating at this temperature, and what happens is the electrodeposition process of metal 。



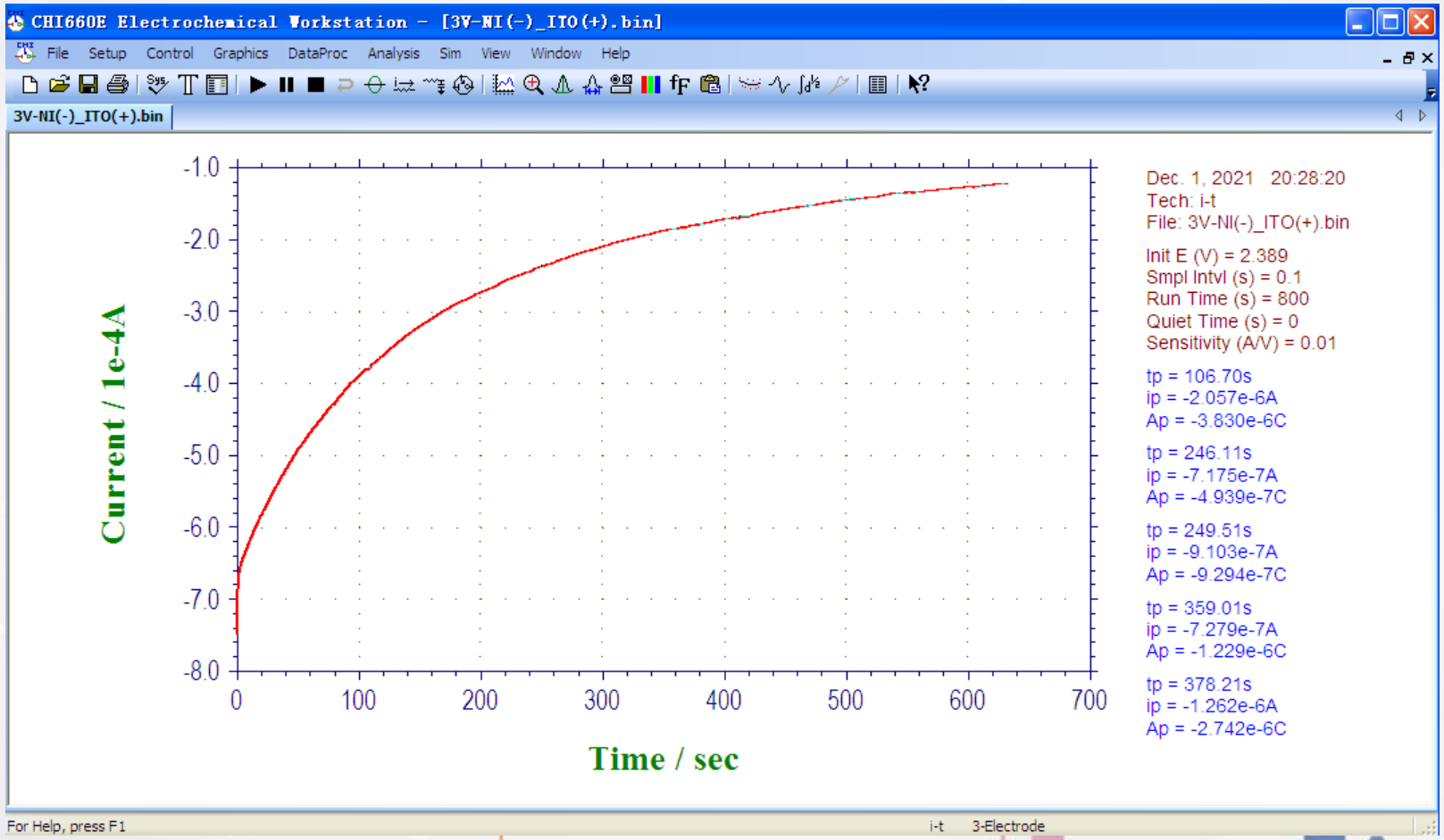
1. Measuring current - time variation - electrochemical workstation

Research Background
Experimental Principle
Experiment Content
Data Processing
Summary



1. Measuring current - time variation - electrochemical workstation

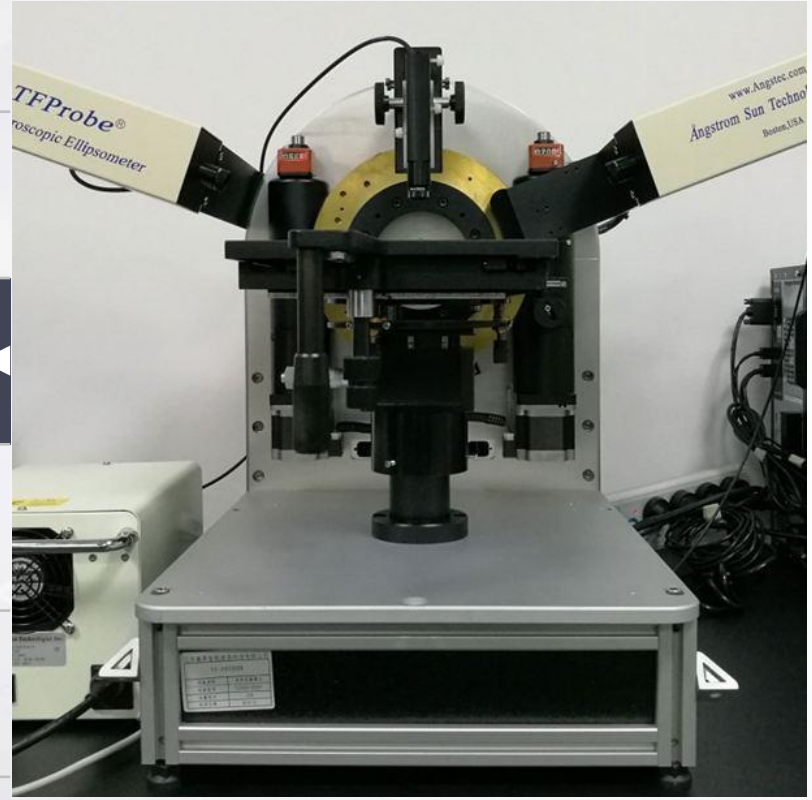
Research Background
Experimental Principle
Experiment Content
Data Processing
Summary

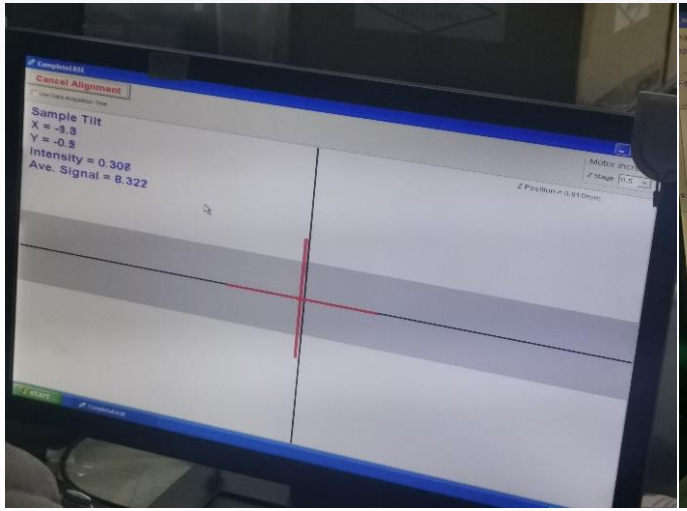


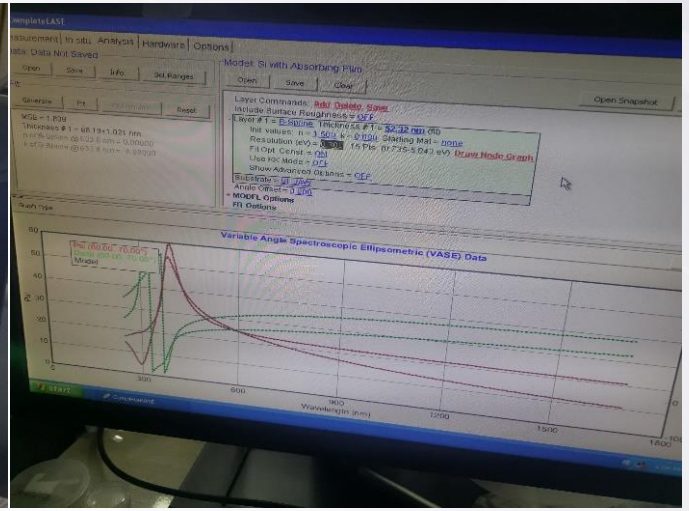
电流以指数形式衰减，变色稳定后趋于零

2. Measuring film thickness - ellipsometer

Research Background
Experimental Principle
Experiment Content
Data Processing
Summary







同一片薄膜，不同位置测量三次膜厚，取平均值。

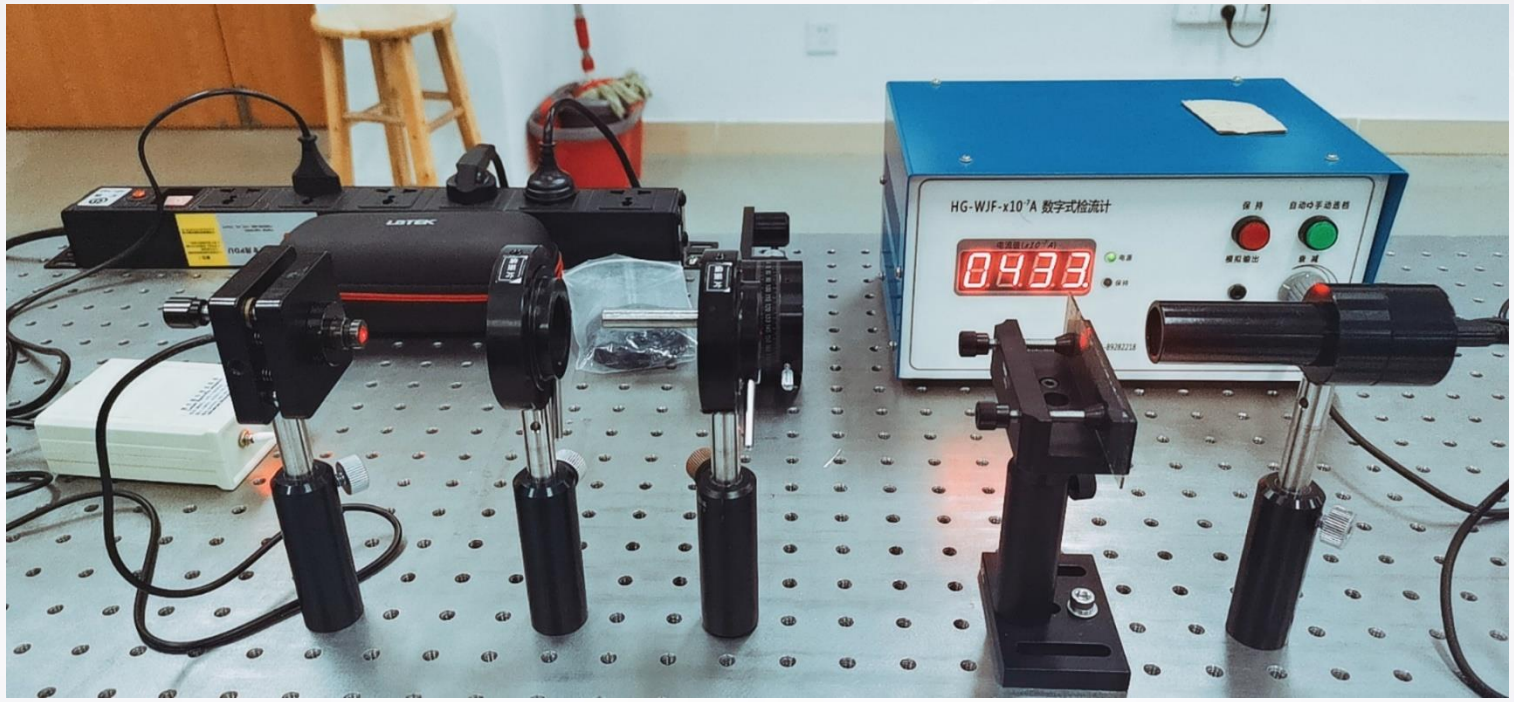
Research Background
Experimental Principle
Experiment Content
Data Processing
Summary

3. Measurement of light intensity change -- laser dual polarization transmission light path

用氦氖激光器产生波长632.8nm的红光，通过双偏振片使入射光为偏折光并调节光强。用光强计测量透过光强

Research Background
Experimental Principle
Experiment Content
Data Processing
Summary

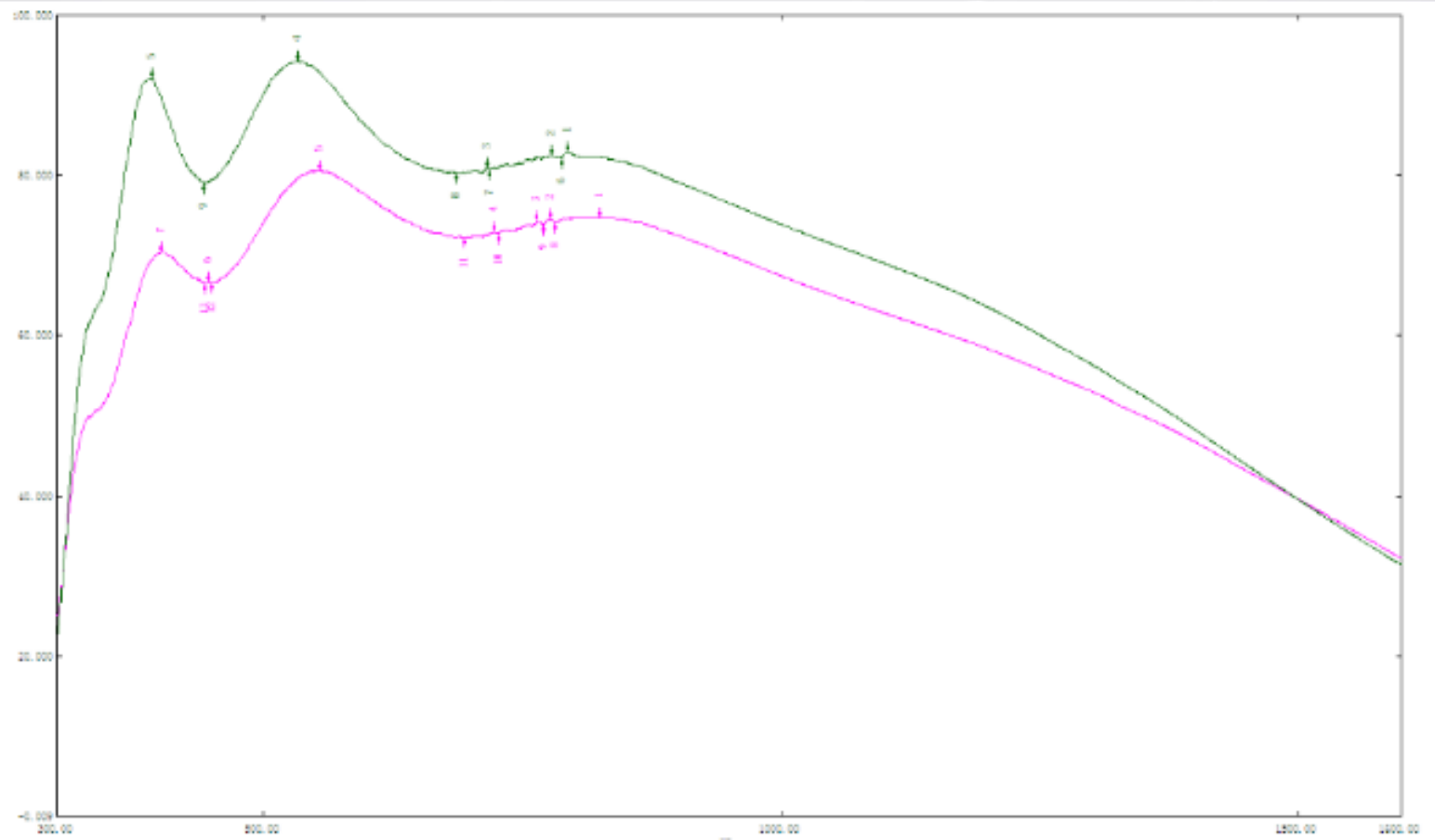
3. Measurement of light intensity change -- laser dual polarization transmission light path



After each discoloration, wait until the glass is completely dry and clamp it perpendicular to the optical axis. The transmission light intensity of the same film is measured for 5 times at different positions, and the average value is taken.

4. Measuring transmission spectrum (spectrometer)

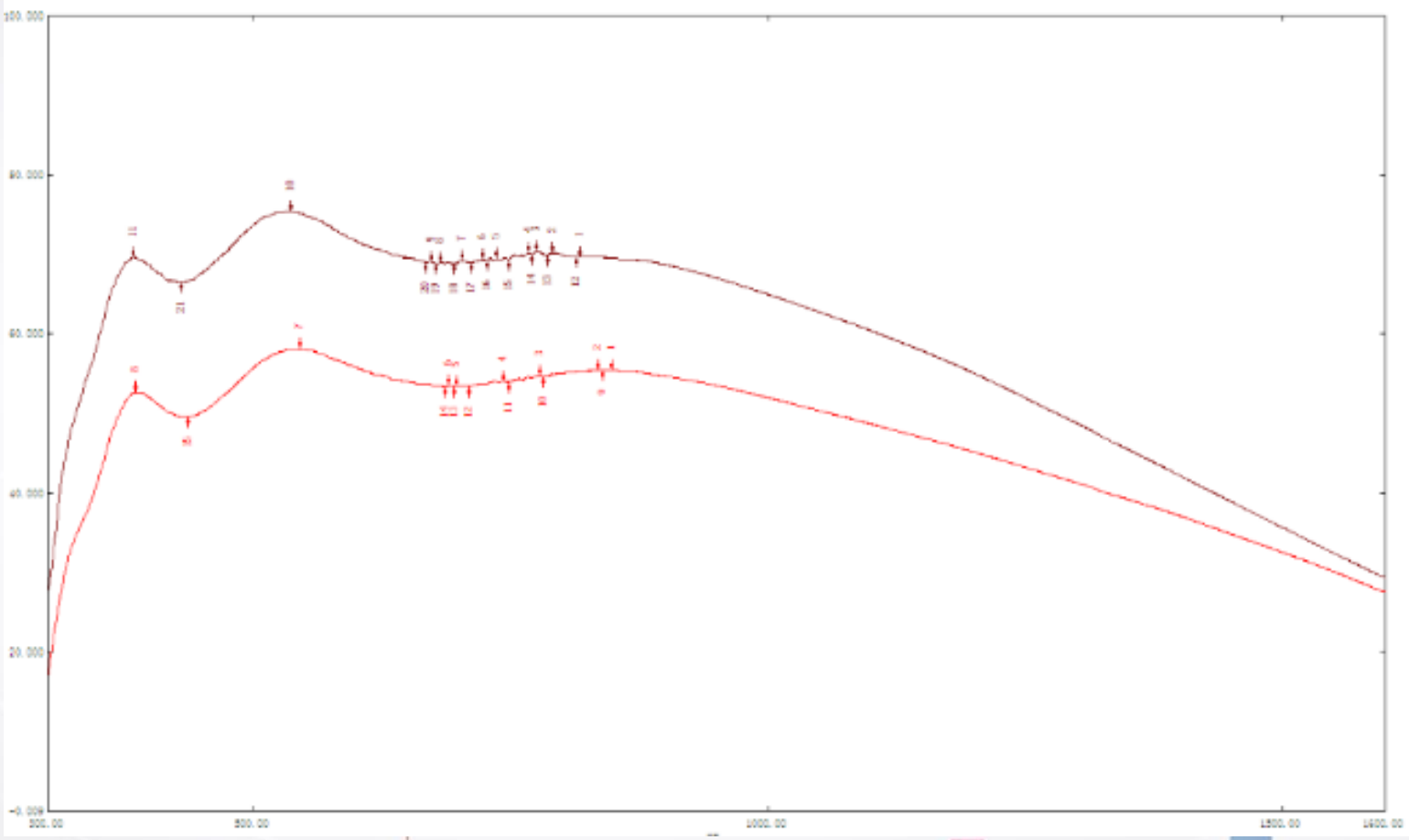
Research Background
Experimental Principle
Experiment Content
Data Processing
Summary



Transmission spectrum of WO3 (upper: faded state, lower: colored state)

4. Measuring transmission spectrum (spectrometer)

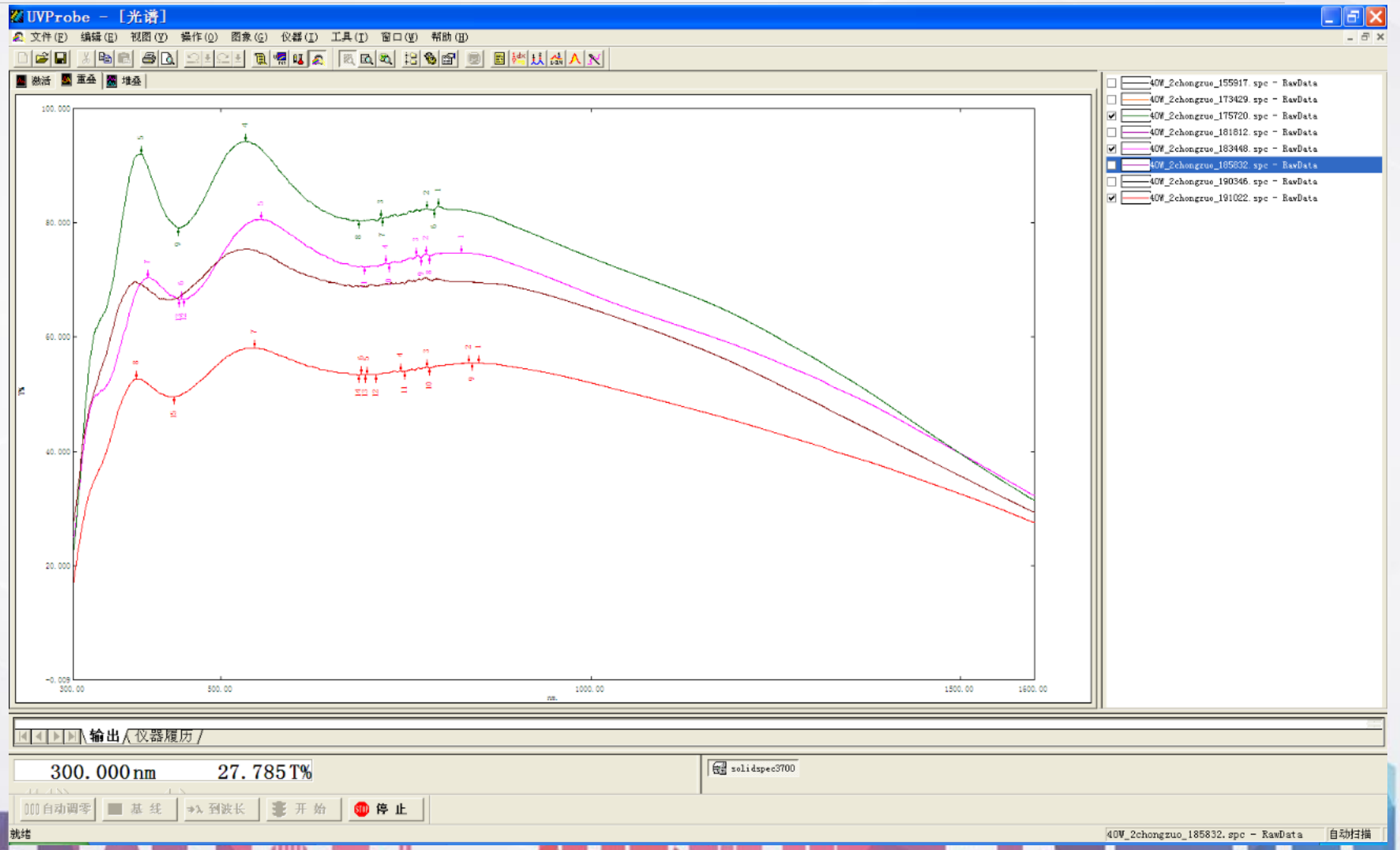
Research Background
Experimental Principle
Experiment Content
Data Processing
Summary



Transmission spectrum of NiO (upper: faded state, lower: colored state）

4. Measuring transmission spectrum (spectrometer)

Research Background
Experimental Principle
Experiment Content
Data Processing
Summary



Contents

目录

1 Research background

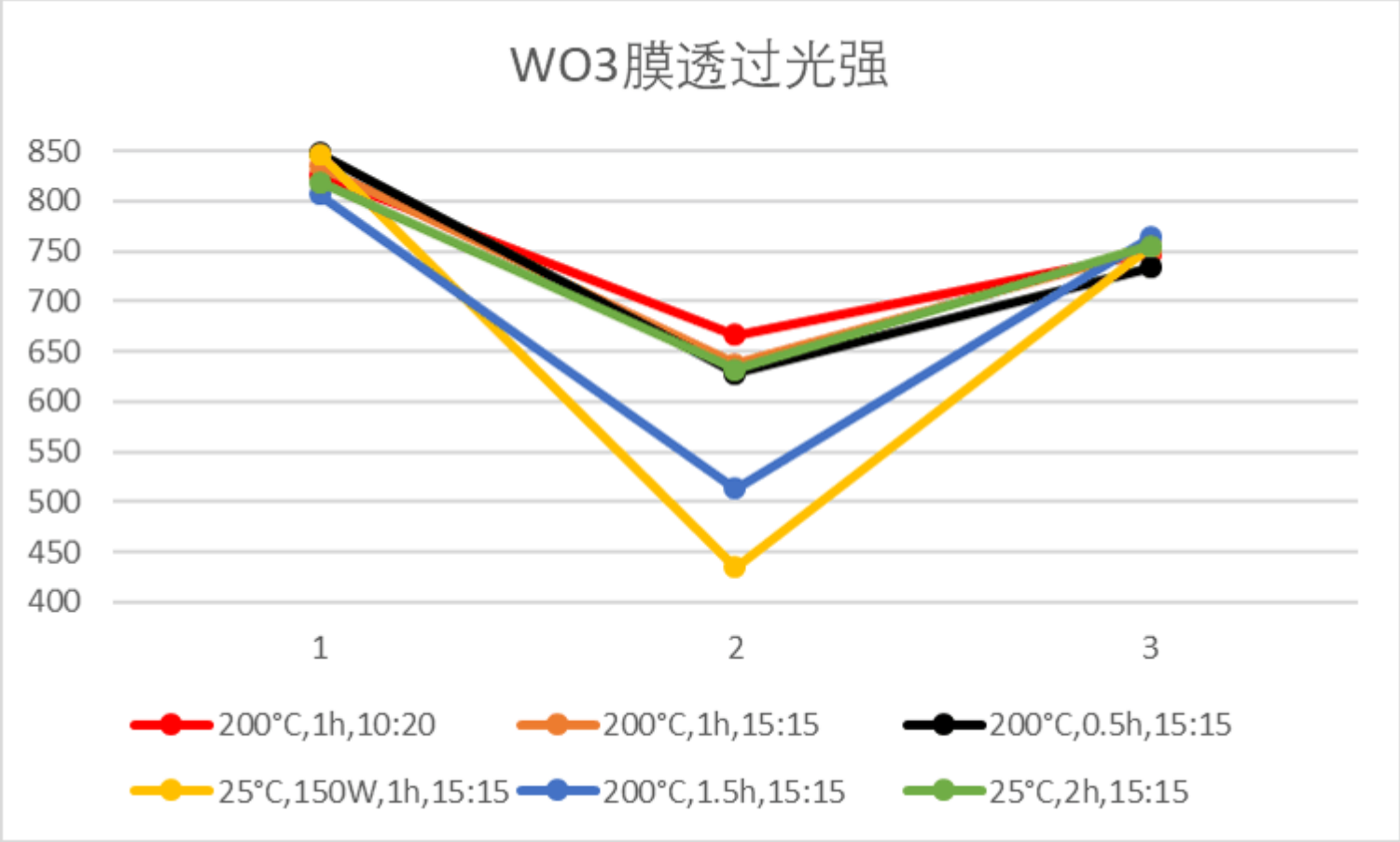
2 Experimental principle

3 Experiment content

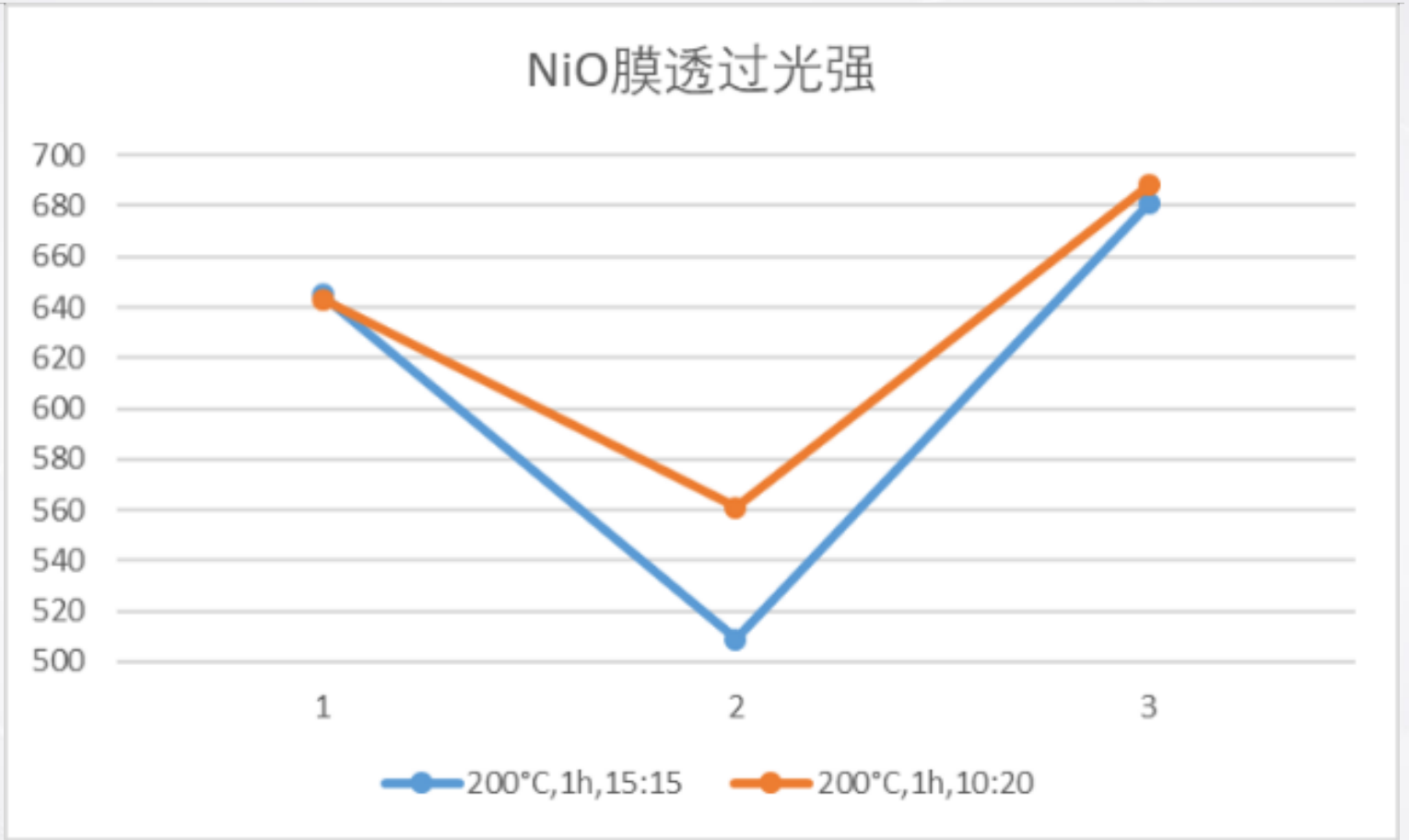
4 Data processing

5 Summary

1. WO3 transmission light intensity change



2. Change of NiO transmission light intensity



3. WO3 recyclability

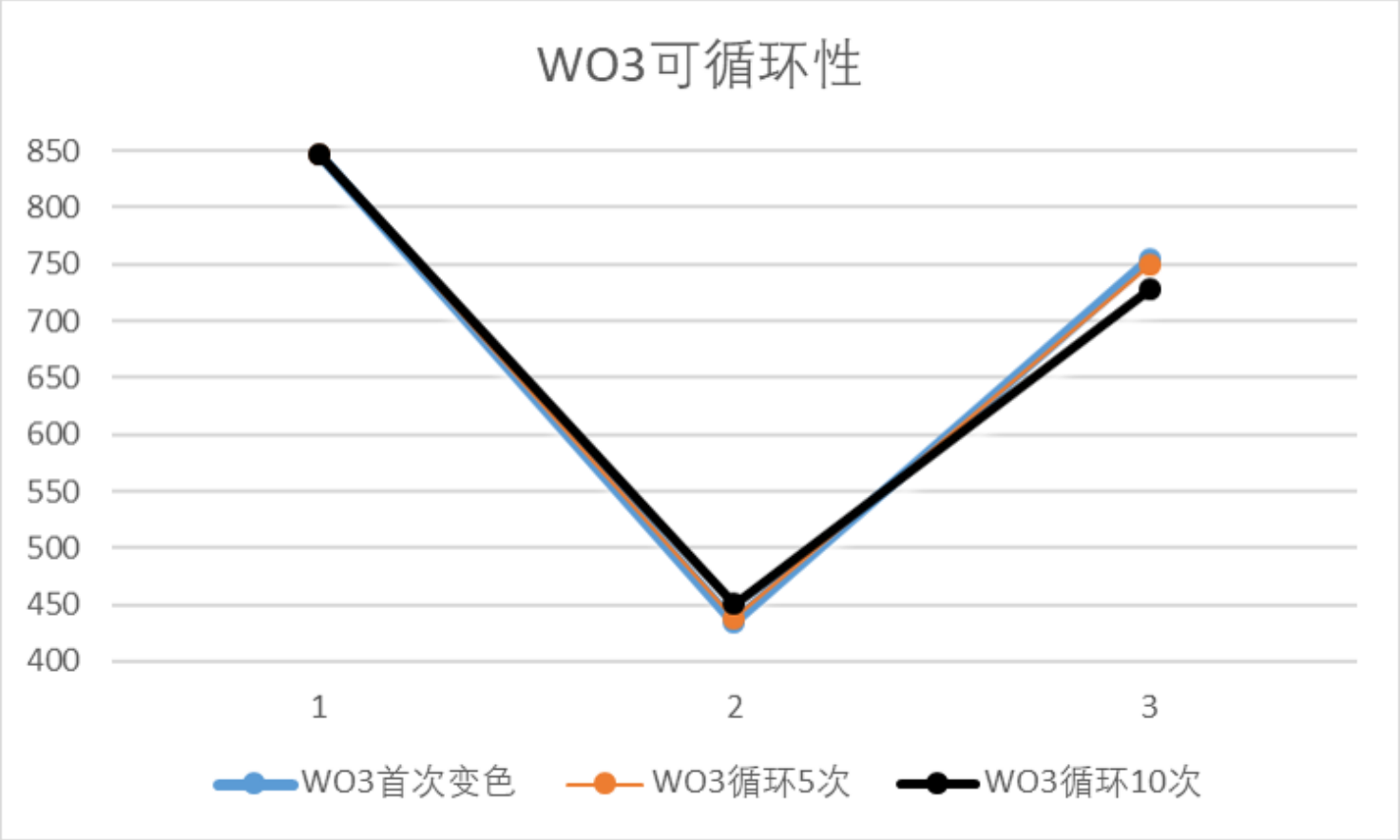
Research Background

Experimental Principle

Experiment Content

Data Processing

Summary



4. Relative variation and circulation coefficient of light intensity

parameter	Film thickness/nm	Relative change of light intensity/colored light intensity	Circulation coefficient
W03-25℃-1h-15:15（150W）	64.53±0.709	0.9471	0.77427
W03-25℃-2h-15:15	57.00±0.184	0.3959	0.65775
W03-200℃-1h-10:20	50.77±0.559	0.2384	0.50943
W03-200℃-1.5h-15:15	58.04±0.175	0.5731	0.85374
W03-200℃-1h-15:15	54.91±0.194	0.3088	0.57868
W03-200℃-0.5h-15:15	46.57±0.335	0.1903	0.48182
Ni0-200℃-1h-15:15	53.85±0.105	0.3379	0.79070
Ni0-200℃-1h-10:20	52.62±0.060	0.2264	0.64567

Contents

目录

1 Research background

2 Experimental principle

3 Experiment content

4 Data processing

5 Summary

Work summary

1. NiO and WO3 amorphous films and electrolyte solutions were prepared under different sputtering conditions
2. The best working voltage is 4V, and the power on time is about 1min
3. The color change range of NiO and WO3 is mainly in the visible light band, independent of the polarization direction
4. Sputtering power, sputtering time and argon oxygen ratio mainly affect the film thickness
5. Temperature will affect the roughness and porosity of the film
6. Within a certain range, the thicker and looser the membrane is, the stronger the ability of ion implantation and extraction is, and the better the discoloration effect and circulation are.

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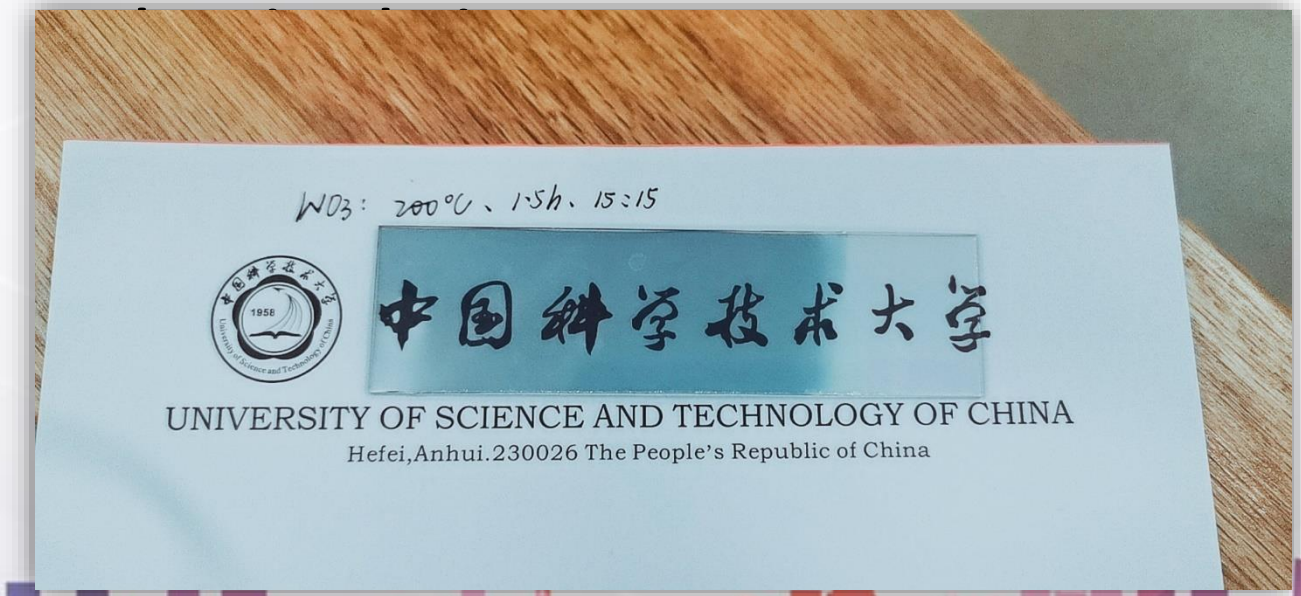
①The variables such as coating temperature, coating thickness and doping elements are further explored

②Consider other discoloring materials and electrolyte conductors

③Explore the possibility of making large area solid-state color



Thanks for watching

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