Fabrication and microscopic optical characterization of metal-oxide based nanostructures

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**FABRICATION AND MICROSCOPIC OPTICAL
CHARACTERIZATION OF METAL-OXIDE BASED
NANOSTRUCTURES**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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in fulfillment of the requirement for the degree of
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ABSTRACT

To date, low-dimensional metal-oxide nanomaterials have attracted intense interests of a great many researchers. In order to better explore the function of such nanostructures in technological applications, it is necessary to understand their characteristics. Most current researches are based mainly on ensemble-averaged measurements, where a large number of nanomaterials are studied and the average responses are recorded. These experiments yield only polydisperse-collective effects, which very often are different from the intrinsic or fundamental properties of the nanomaterials. Some unique properties of nanomaterials cannot be observed because of the large variations in particle shape, orientation, size, and surface defects. The main goal of this research is to fabricate and test the physical properties of individual nanostructures.

In this dissertation, several metal-oxide nanostructures, V_2O_5 nanoribbons, MoO_3 nanoflakes, ZnO nanowires and Fe_2O_3 nanoflakes are fabricated via the thermal evaporation method. The physical, especially optical, properties are investigated by the micro-photoluminescence and Raman scattering techniques. Waveguiding effects and morphology-induced anomalous polarized Raman properties are investigated on waveguiding V_2O_5 nanoribbons. By controlling the orientational arrangement of MoO_3 nanoflakes, we demonstrate the anisotropic electrical/optical properties and edge-preferred defect distributions. Local exciton-longitudinal optical phonon interaction in a single ZnO nanowire is suppressed by mechanical deformation. In

addition, we proposed a mechanism to elucidate the ultraviolet induced change of surface wettability of ensembled Fe_2O_3 nanoflakes.

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Chapter 1 Introduction

“I would like to describe a field, in which little has been done, but in which an enormous amount can be done in principle. This field is not quite the same as the others in that it will not tell us much of fundamental physics but it is more like solid-state physics in the sense that it might tell us much of great interest about the strange phenomena that occur in complex situations. Furthermore, a point that is most important is that it would have an enormous number of technical applications.”

Richard P. Feynman,¹ December 29th 1959

1.1 Nanotechnology and Science of Small

Figure 1.1 Minimum size in a chip over the years.²

Richard P. Feynman’s classic talk, “There’s plenty of Room at the Bottom”, was considered as the beginning of the nanoscience and nanotechnology. Later in 1965,

Gordon E. Moore, the co-founder of Intel, states that the number of transistors on a chip will double about every two years. Till now, “Moore’s Law” (**Figure 1.1**) has required that Feynman’s foresight will produce nanoscale circuits.

A nanostructure is defined on the scale of one to a few hundred nanometers-small indeed, but much larger than single molecule. Nanoscience and technology provide us a chance to optimize and minimize the traditional devices. Charles M. Lieber’s group reported that nanowire can be used as tiny building blocks for nanoscale electronics and optoelectronics (**Figure 1.2**)³⁻⁷. Besides, with two naturally faceted end faces acting as reflecting mirrors, a resonance Fabry-Perot cavity can be formed in an individual nanowire. Based on this, electrically and optically driven nanowire lasers were successfully fabricated⁸⁻⁹. Recently, multi-quantum-well (MQW) nanowire heterostructures have also been rationally synthesized for wavelength-controllable nanolasers¹⁰. More excitingly, using a hybrid plasmonic waveguide consisting of a high-gain CdS nanowire, the smallest laser was created by Zhang’s group¹¹. "This work shatters traditional notions of laser limits, and makes a major advance toward applications in the biomedical, communications and computing fields." The nanotube radio, demonstrated by Alex Zettl¹², can function as a radio that detects and plays songs: a single carbon nanotube tunes in a broadcast signal, amplifies it, converts it to an audio signal and then sends it to an external speaker in a form that the human ear can readily recognize.

Compared with the crystal structures, dimensionality plays a critical role in determining the properties of nanomaterials. When the size of nanomaterials is

comparable to the wavelength associated with electrons or photons, the system may display quite different electrical or optical phenomena as those described by classical physics. This new nanoscience concerns a scale far beyond what can be called microscopic but not yet large enough to be considered macroscopic. It is the science of the mesoscale. In this case, nanomaterials are expected to show some unique properties which are governed by a complex and rich combination of classical physics and quantum mechanics. Investigating their intriguing behavior is of crucial importance in building practical devices. For example, Lu et al.¹³ observed well-defined Coulomb diamonds as expected for transport through an individual single-electron transistor in Ge/Si core/shell nanowire heterostructures. van Vugt¹⁴ discovered that subwavelength ($\lambda/9$) dispersionless guiding in ZnSe nanowire and significant slowing of the propagating light by 90% ($c/8$) due to enhanced light matter interaction close to the exciton resonance (**Figure 1.3**).

Figure 1.2 Crisscrossed semiconductor nanowires can be used as building blocks for memory switches.^{7,15}

Figure 1.3 Group index obtained by mode dispersions from a ZnSe nanowire with radius of 150 nm. Inset: Mode dispersion obtained from waveguiding tip emission spectrum.¹⁴

Besides the investigation of individual nanostructures, the ensembles of nanomaterials open up fantastic vistas for modifying the surface properties and even designing new functional structures that in principle do not exist in nature. It is found that the striking adhesive strength in gecko setae¹⁶⁻¹⁷, strong superhydrophobic force on water strider's leg¹⁸ and the water-collecting ability of the spider silk¹⁹ etc., are all related to the unique micro- and nanostructures on the surfaces. Jaime Gomez Rivas' Group has reported that the good alignment of the nanowires results in a series of interesting optical properties, such as strong antireflection²⁰, anisotropic scattering²¹ and birefringence²²⁻²³. Furthermore, Kenji Hata²⁴ found that the vertically aligned single-walled carbon nanotubes behave most similarly to a blackbody, which could

absorb all incident light.

1.2 Scope of Thesis Work

Metal oxides, as the most commonly encountered solids, occupy a rather important position in the study of material sciences. In contrast to carbon nanostructures, which may be either semiconducting or metallic, the properties of metal-oxide nanomaterials are always determined by the properties of the material they are made of. In this thesis, several kinds of metal-oxide nanomaterials, V_2O_5 nanoribbon, MoO_3 , Fe_2O_3 nanoflakes and ZnO nanowires, were synthesized by thermal oxidation. The unique physical characterizations, especially the optical properties, were investigated due to their limited size, morphology and structure. Chapter 2 describes the instrumentations for performing the microscopy and spectroscopy for individual nanostructures. This chapter also introduces some basic concepts which will be used in the next chapters. Chapter 3 discusses the photoluminescence and waveguiding properties of individual V_2O_5 nanoribbons. The anomalous polarized Raman properties on the waveguiding nanoribbon are investigated in Chapter 4. In Chapter 5, polarized Raman imaging is used to characterize the defect distribution on MoO_3 nanoflakes. Besides, the enhanced field emission on erected MoO_3 nanoflakes are reported here. In Chapter 6, we demonstrate that mechanical deformation-induced change of phonon-exciton interaction in ZnO nanowire. In Chapter 7, UV effects on surface wettability of Fe_2O_3 nanofilms are presented. In the last chapter the conclusions are drawn and some recommendations are made for future work.

Chapter 2 Background and Experimental Techniques

In this chapter, the theoretical background for an understanding of the experiments and basic principle of the characterization instruments will be discussed: how can we get low-dimensional nanomaterials, how can we bridge between the nanoworld and the macroworld, and what is expected of them?

2.1 Growth Mechanism of Anisotropic Nanostructures

Under favorable conditions, the external surface of crystal is always bounded by a set of plane faces. Each surface is assigned a free energy as being reciprocally determined by the perpendicular distance from the point of origin of the crystal to this face. The crystals adopt a morphology which minimizes the total surface energy. So the high index faces grow very quickly and soon disappear. The general rule relating morphology to growth velocity is that “fast-growing faces disappear, slow-growing faces remain”²⁵. The anisotropic growth will result into confined crystalline morphology.

Based on this rule, several kinds of bottom-up strategies can be used to modify the surface energy at certain crystalline faces to fabricate low-dimensional anisotropic (confinement) nanomaterials²⁶⁻²⁷:

- (i) growth of an intrinsically anisotropic crystallographic structure. For α - MoO_3 crystals, it is found that growth rate (r_{hkl}) variation in all three principal

directions: $r_{001} \gg r_{100} \gg r_{010}$, resulting $\langle 010 \rangle$ oriented nanosheets. Besides, with external bonding capacity, Zeng²⁸ could switch on and off the crystal growth along a specific crystallographic direction at a particular time. So that crystals with complex nanostructures can be engineered (**Figure 2.1**). Based on very similar principle, by employing certain additives that can preferentially adsorb on specific crystallographic planes, growth rate of various crystallographic planes in Cu_2O can also be changed, resulting in crystals with different final morphologies²⁹.

Figure 2.1 TEM image of a four-armed $\alpha\text{-MoO}_3$ nanostructure. Inset: growth mechanism of the nanomaterial.²⁸

- (ii) the use of various templates with low-dimensional morphologies to direct the formation of low-dimensional nanostructures. Charles R. Martin³⁰⁻³¹ proposed that the pores in the nanoporous membranes can be used as templates for

forming the desired material. Combined the concepts of sol-gel synthesis and template preparation of nanomaterials, nanotubes and fibrils composed of a variety of materials including metals, polymers, carbons, and other materials have been successfully fabricated.

- (iii) the introduction of a liquid/solid interface or an appropriate capping reagent to reduce the symmetry of a seed and kinetically control the growth rates of various facets of materials. The vapor-liquid-solid (VLS) process, as an elegant method, is widely used to fabricate nanowire structures. This process contains two important steps: expansion of the nanowire base and growth of the nanowire. The schematic illustration is shown in **Figure 2.2**. Thermodynamically, the transformation of the seed at the initial phase is promoted by the difference of Gibbs free energies, which is related to the liquid droplet composition and its size³². At equilibrium, the system can be written:

Figure 2.2 The evolution of the droplet and wire shape.³³

$$\sigma_l \cos(\beta) = \sigma_s \cos(\alpha) - \sigma_{ls} . \quad (2-1)$$

Here, σ_l is the surface tension of the catalyst droplet; σ_s is the surface tension of the solid; and σ_{ls} is the surface tension of the liquid-solid interface.

To form uniform nanowire, the horizontal components of the surface forces should cancel out, with $\alpha = 90^\circ$, so we get

$$\sigma_1 \cos(\beta) = -\sigma_{ls}. \quad (2-2)$$

In this case, the growth of nanowire is kinetically controlled by

$$v_s = \alpha_{ls} (\mu_l - \mu_s),^{34} \quad (2-3)$$

where α_{ls} is the kinetic rate coefficient, and μ is the chemical potential. Till now, many different types of compound nanowires have been fabricated using metal as catalyst or self-catalyst method.

Considering the unique structural one-dimensionality and possible quantum confinement effects in two dimensions, semiconductor nanowires exhibit many novel electronic and optical properties and are expected to play a critical role in future electronic and optoelectronic devices.

2.2 Characterization

2.2.1 Optical Microscopy

“As Galileo's Siderus nuncius did for the telescope, the Micrographia presented to the reader a visual cornucopia of the wonders of the microscopic world. Hooke was able to demonstrate the immense possibilities of using the microscope as a tool in scientific research.”

Robert Hooke. "Micrographia", 1665.

The contributions of optical microscopy continue into the present, even as the systems of interest approach nanometer size. What makes optical microscopy so useful is that:

it doesn't irreversibly alter the electronic or crystalline structure of the material which it interacts with, allowing observation in situ. Moreover, light is cheap, abundant, and can be manipulated with common and relatively inexpensive laboratory hardware.³⁵

Two different directions have been developed to utilize the optical microscopy to characterize nanomaterials: near-field technology and far-field technology. The principles on which near-field optics is developed are related to the physics of evanescent electromagnetic waves, which can build up around metallic or dielectric pointed tips³⁶. Till now, a resolution of ~12 nm (at $\lambda=514$ nm), which approaches the limit imposed by the penetration depth of evanescent fields, has been achieved by evanescent wave coupling between the nanometer-sized detector and subwavelength size object deposited on a surface.³⁷⁻³⁸

The confocal microscopy is one of the most prevalent far-field techniques. Compared to near-field technology, confocal technique is an easy, rapid, and inexpensive way, which is widely used to characterize the micro-properties. By placing a pinhole in front of the detector, the out-of-focus information can be rejected, so that the images have a high signal-to-noise ratio and better spatial resolution (**Figure 2.3**). The price of single-point detection is being able to measure only one point at a time. Even if it seemed more elegant to deflect the weightless light than to move a massive specimen, Marvin Minsky proposed to keep the optics fixed and move the stage to avoid the problem of maintaining the three-dimensional alignment³⁹. This is why a confocal microscope must scan the specimen point by point. A spatial resolution of half the excitation wavelength can be produced with a confocal microscope in conjunction

with a high-resolution piezoelectric stage.

Figure 2.3 Principle of confocal microscopy from Marvin Minsky.

At first glance, the idea that far-field optical microscopy can contribute to nanotechnology may appear absurd because of the diffraction limit. However, it enables the optical characterization of individual nanostructures by using a focused beam spot smaller than the distance between adjacent nanomaterials.

Combined with polarized Raman analyses, Yang⁴⁰ reported that confocal microscopy demonstrates the ability to gain information on the nanowire's phase, growth direction, and radial crystallographic orientation. Leigh M. Smith's group⁴¹⁻⁴² utilized spatially resolved polarized low temperature photoluminescence (PL) and Raman to probe the electronic states and structural symmetries of individual nanosheets. The waveguiding eigenmodes and lasing from single ZnO nanowires could also be observed by confocal microscopy.⁴³⁻⁴⁵ Besides, time-resolved/temperature-dependent micro-photo luminescence is a novel area which will provide new insights and new understanding of the complex dynamic behaviors in single nanostructures⁴⁶⁻⁴⁸.

2.2.2 Electron Microscopy

According to Abbe's limit, the resolution is directly related to the illumination wavelength. The scanning electron microscope (SEM) is a type of microscope that uses electrons rather than visible light to form an image. So a better spatial resolution can be expected.

Figure 2.4 Scanning electron microscope.

Figure 2.4 is a vertical profile graph of a SEM. The electron beam is generated by heating the filament in the electron gun. The anode can change the electron energy. Condenser lens changes probe current continuously. While the zoom condenser lens will keep focus during probe current change. Objective lens aperture is used to change

probe current stepwise. Scan coil scans electron probe over specimen to form an image. Objective lens focuses the electron beam to the specimen.

When the electron beam strikes the sample, both photon and electron (backscattered and secondary electrons as shown in **Figure 2.5**) can be excited. The backscattered electrons have high energy and are detected with a backscattered electron detector located above the specimen. While the secondary electrons have low energy of less than 50 eV and are collected by a secondary electron detector. In this way, the composition contrast (backscattered electrons) and surface morphology (secondary electrons) can be observed.

Figure 2.5 The interaction between incident electrons and specimen.

Like SEM, transmission electron microscope (TEM) also uses electron beam to form an image. But the detected electrons are transmitted primary electron which can penetrate through the specimen, so the resolution is not limited by the issues regarding secondary electrons. A much higher spatial resolution can be provided by TEM. In

addition, when the electron beam passes through the sample, electrons can be coherently scattered (diffracted). The diffracted electrons can be used to identify the crystallographic characteristics, symmetry, lattice parameters and so on.⁴⁹

2.2.3 Raman Scattering Spectroscopy

Even if TEM is an elaborate technique to investigate the structural and chemical information in nanosystem, it is time-consuming and requires high-vacuum. Special care must also be taken to avoid electron beam-induced damage or carbon deposition that affects the measured properties of the specimen. In this case, Raman scattering spectroscopy is a promising tool to probe the chemical composition, physical state, and lattice dynamics of samples in a simple, fast and nondestructive manner.

2.2.3.1 Principle of Raman Scattering

Figure 2.6 Spontaneous light scattering. (a) Experimental set up. (b) Typical observed spectrum.⁵⁰

Scattering is one of the most general physical processes when light interacts with matter. In general, the scattered spectrum (**Figure 2.6**) shows several parts. Rayleigh scattering is the strong elastic scattering of light with no frequency shift. The wing of the Rayleigh line can be observed, resulting from fluctuations in the orientation of anisotropic molecules with an anisotropic polarizability tensor. Brillouin scattering is an interaction of light with low frequency quasiparticles, such as magnetic spin waves (magnons) and acoustic phonons. The Brillouin frequency shift is very small ($\sim 0.1 \text{ cm}^{-1}$) and is normally detected with an interferometer.

Discovered by C. V. Raman⁵¹, Raman scattering results from the interaction of light with the vibrational or rotational transitions in molecules. Considering a plane incident wave described by

$$\vec{E}(\vec{r}, t) = \vec{A}_i(\vec{k}_i, \omega_i) e^{i(\vec{k}_i \vec{r} - \omega_i t)} \quad (2-4)$$

in the material, an induced polarization $\vec{P}(\vec{r}, t)$ will be obtained from

$$\vec{P}(\vec{r}, t) = \chi(\vec{k}_i, \omega_i) \vec{E}(\vec{r}, t) = \chi(\vec{k}_i, \omega_i) \vec{A}_i(\vec{k}_i, \omega_i) e^{i(\vec{k}_i \vec{r} - \omega_i t)}. \quad (2-5)$$

Here, $\chi(\vec{k}_i, \omega_i)$ denotes a tensor of the second-order electric susceptibility. It can be taken as a function of atomic displacements

$$\vec{u}(\vec{r}, t) = \vec{u}(\vec{q}, \omega_0) e^{\pm i(\vec{q} \vec{r} - \omega_0 t)} \quad (2-6)$$

associated with the vibration of crystals (phonon)⁵². So we can get

$$\chi(\vec{k}_i, \omega_i, Q) = \chi_0(\vec{k}_i, \omega_i) + (\partial \chi / \partial \vec{u})_0 \vec{u}(\vec{r}, t) + \dots \quad (2-7)$$

Then, Eq. (2-5) can be expressed as

$$\vec{P}(\vec{r}, t, Q) = \vec{P}_0(\vec{r}, t) + \vec{P}_i(\vec{r}, t, Q), \quad (2-8)$$

$$\text{where } \vec{P}_0(\vec{r}, t) = \chi_0(\vec{k}_i, \omega_i) \vec{A}_i(\vec{k}_i, \omega_i) e^{i(\vec{k}_i \vec{r} - \omega_i t)}, \quad (2-9)$$

$$\text{and } \bar{P}_i(\bar{r}, t, \bar{Q}) = (\partial\chi / \partial\bar{u})_0 \bar{u}(\bar{r}, t) \bar{A}_i(\bar{k}_i, \omega_i) e^{i[(\bar{k}_i \pm \bar{q})\bar{r} - (\omega_i \pm \omega_0)t]}. \quad (2-10)$$

From these expressions, we can see that $\bar{P}_0(\bar{r}, t)$ is a polarization vibrating in phase with incident light. In contrast, $\bar{P}_i(\bar{r}, t, \bar{Q})$ is induced by the phonon and contains two kinds of frequencies: Stokes Raman frequency $\omega_s = \omega_i - \omega_0$ with wavevector $\bar{k}_s = \bar{k}_i - \bar{q}$ and anti-Stokes Raman frequency $\omega_{as} = \omega_i + \omega_0$ with wavevector $\bar{k}_{as} = \bar{k}_i + \bar{q}$.

If we consider the polarization of scattering signal $\bar{A}_s$, the scattered intensity is proportional to

$$I_s \propto \left| \bar{A}_s (\partial\chi / \partial\bar{u})_0 \bar{u} \bar{A}_i \right|^2. \quad (2-11)$$

Here, we introduce a parameter $\mathfrak{R} = (\partial\chi / \partial\bar{u})_0 \bar{u}$, which is known as the Raman tensor⁵³. The rigorous derivations on the Raman tensors in crystals have been solved with the help of group theory⁵⁴. Such that using $I_s \propto \left| \bar{A}_s \mathfrak{R} \bar{A}_i \right|^2$ (the selection rules), the azimuthally dependence of Raman-active phonons or the crystalline orientation can be determined.

2.2.3.2 Instrumentation

There are two Raman spectrometers in our laboratory: i) Witec and ii) Renishaw in Via Raman microscope.

- i) Witec Confocal Raman Microscope. **Figure 2.7** shows the picture of the system with each component labeled. A double-frequency Nd:YAG laser (532 nm) and 457 nm laser are used as the laser source, which can be coupled to a 3.5 μm core-diameter single mode optical fiber. Reflected by a dichromic

mirror, the excitation light passes through a $\lambda/2$ plate so that its polarization can be rotated. Then, it is focused on the sample with an objective.

Figure 2.7 Setup of the Witec Ramam system.

The sample is placed onto a translation stage, which can be moved coarsely in a horizontal plane. It could also be finely moved in three dimensions. The scattered light is directed to a grating and detected using a thermoelectrically-cooled CCD. The polarization of the scattered signal is analyzed by the analyzer. While the Rayleigh scattering is 'blocked' by the

notch filters, the stage movement and data acquisition are controlled using ScanCtrl Spectroscopy Plus software from WITec GmbH, Germany. The signal can also be collected by the downside optical path. In this way, the front scattering or micro-transmission is accessible. The propagation property in nanomaterials is investigated by independent selection of the excitation and collection points.

Figure 2.8 A picture of the Renishaw inVia Raman Microscope.

- ii) Renishaw inVia Raman Microscope, armed with three laser sources (325 nm, 532 nm, and 785 nm), allows us to detect resonance Raman or surface enhanced Raman scattering. The instrument setup is shown in **Figure 2.8**. Furthermore, by adjusting the mirrors (bottom left, bottom right and top left ones) the laser focus point is moved, while only those signals coming from the

center of the microscope can be collected (**Figure 2.9**). The confocal pinhole in optic route ensures a high lateral resolution. So that, remote Raman spectra⁵⁵ and waveguiding⁵⁶ can be tested in the backscattering configuration.

Figure 2.9 Schematic illustration of remote excitation. Laser can be focused at a distance away from the center, while by the confocal pinhole, only those signals from the center can be collected.

2.2.3 Contact Angle

In addition to morphology and crystalline structure of the individual nanomaterials, we also investigated the surface wettability which could be modified by the nanostructure ensembles. The central characteristic of the wettability is the equilibrium contact angle, θ , which is determined by the angle between the tangents to the liquid-fluid interface and to the solid at the line of contact between the three phases (**Figure 2.10**).

The contact angle on an ideal surface was predicted by Young equation⁵⁷:

$$\cos \theta_Y = \frac{\sigma_{sf} - \sigma_{sl}}{\sigma_{lf}}, \quad (2-12)$$

where σ_{sf} , σ_{sl} , and σ_{lf} are the solid-fluid, solid-liquid, and solid-fluid interfacial

tensions. The Young contact angle represents the minimal-Gibbs-energy state of the smooth and homogeneous system.

Figure 2.10 Two examples of graphical demonstrations of the contact angle.⁵⁸

If the solid surface is rough but still chemically homogeneous (the liquid completely fills the grooves of the rough surface as shown in **Figure 2.11**), the additional surface area produces an increase in the surface energy:

$$dE = r(\sigma_{sl} - \sigma_{sf})dx + \sigma_{lf}dx \cos \theta_w . \quad (2-13)$$

Figure 2.11 The bottom rim of a droplet on a rough surface.

Here, r is the roughness factor and defined by: $r = \frac{\text{actual surface}}{\text{projected area}}$.

At equilibrium condition, $dE=0$. So we get:

$$\cos \theta_w = r \frac{\sigma_{sf} - \sigma_{sl}}{\sigma_{lf}} = r \cos \theta_Y . \quad (2-14)$$

From this formula and **Figure 2.12**, we can see that the apparent contact angle θ_w

(the wetting properties of a substance) is much related to the surface roughness: the wetting is enhanced by roughness for hydrophilic surfaces ($\theta_Y < 90^\circ$), conversely, lessened for hydrophobic surfaces ($\theta_Y > 90^\circ$). In addition, Cassie⁶⁰ considered chemically heterogeneous surface, and revealed:

$$\cos \theta_C = \sum_i x_i \cos \theta_{Y_i}, \quad (2-15)$$

Figure 2.12 The predictions of the Wenzel equation with different surface roughness.⁶¹

here, x_i is the area fraction characterized by a given chemistry. In this way, ultra-hydrophobic (self-cleaning) or ultra-hydrophilic (anti-fog) surfaces can be provided by controlling the surface micro-/nanostructure and the chemical compositions.

Chapter 3 Waveguiding and Photoluminescence Properties on Individual V₂O₅ Nanoribbons

3.1 Introduction

High-density photonic and optoelectronic integration is a natural alternative to electronic infrastructure and is a rapidly growing field.^{9,62-64} Compared to traditional electrical transmission, optical transmission has a very large bandwidth (information capacity) and high speed. Central to progress in this area has been the development of materials and structures that can provide flexibility in connecting various nanophotonic elements. Conventionally, nanoscaled optical fibers are fabricated using a physical drawing process, and have been shown to be promising materials for low-loss optical guiding⁶⁵⁻⁶⁷ and fast detection⁶⁶. Admirable results presented by Yang and co-workers⁶⁸⁻⁶⁹ demonstrate that single-crystalline semiconducting nanoribbons can be successfully used for passive and active photonic integrations. In addition, Lieber's group⁷⁰⁻⁷¹ reported that active nanowires have unique advantages in combination with electronics. Therefore, the fabrication of one-dimensional single-crystalline nanomaterials is of great scientific interest and technological significance, which will bring about the impetus of photonic integration and promote the development of optical information technology and optical-based nanobiosensors.

Divanadium pentoxide (V_2O_5), the most stable form in the vanadium oxide family, has been at the forefront of applied research due to its unique physical and chemical properties. For example, Gu and co-workers⁷² showed that sheets made of entangled vanadium oxide nanofibres behave like artificial muscles (actuators) that contract reversibly under an electrical signal. In addition to its electromechanical properties, V_2O_5 also exhibits excellent photochromic or electrochromic behavior⁷³⁻⁷⁴, upon light irradiation or electrochemical reactions. A number of enabling mechanical and optical properties show that the low-dimensional nanostructures of V_2O_5 are candidate materials for applications in photonics. In this regard, the optical properties of individual V_2O_5 nanoribbons are desirable and significant for our study.

3.2 Experiments and Discussions

3.2.1 Sample Fabrication and Characterization

There are several approaches available for synthesizing nanostructures of vanadium oxides.⁷⁵⁻⁸⁰ It is important to develop a new method with desirable practical attributes such as simplicity, catalyst-free, and not requiring extreme pressure conditions.⁸¹⁻⁸³ In this contribution, we have synthesized divanadium pentoxide nanoribbons using a simple thermal vapor deposition technique under ambient conditions.

A clean piece of vanadium foil ($10 \times 10 \times 0.1$ mm) with a purity of 99.8 % (Lesker) was heated at 660°C under ambient conditions with a piece of Si wafer (with a 200 nm thick, thermally grown SiO_2 layer) covering the foil without the use of catalyst. After the heating process of about 4-10 hours, the sample was allowed to cool down to

room temperature before removal from the furnace. Elongated nanostructures were observed on the side of wafer facing the metal foil.

Figure 3.1 Optical waveguiding effects in V_2O_5 nanoribbon. a) Dark-field image of an as-grown sample. b) Far-field photoluminescence image of a nanoribbon waveguide under laser excitation. The laser is focused to a spot size of 500 nm at the middle of the ribbon. Generated PL (in bottom right corner) is guided to the tip of the ribbon (in top left corner). c) The corresponding optical image.

Representative dark-field optical images (**Figure 3.1a**) revealed that nanoribbons with a typical length of several hundred micrometers, and even up to millimeters, were produced in high yield. The typical topography of the as-grown products was examined using field emission scanning electron microscope (SEM, JEOL JSM-6700F) as shown in **Figure 3.2a**. The ribbons have a rectangular cross-section with a typical width and height of ~ 300 nm and ~ 100 nm, respectively, giving a length-to-width or length-to-height aspect ratio of well over 1000. These nanostructures have excellent cross-section uniformity and smooth surfaces without

pronounced structural defects, making them ideal for low-loss optical waveguides, sensors and interconnects.

Figure 3.2 a) High-magnification SEM images of sample. The inset shows the near-rectangular cross section of a V_2O_5 nanoribbon. b) Raman spectrum of an individual nanoribbon. c) A field emission transmission electron microscopy (FETEM) image of an individual V_2O_5 nanoribbon, with its corresponding selected area electron diffraction (SAED) pattern. d) High-magnification transmission electron microscope image.

Earlier works described the complicated structure of V_2O_5 as layer slabs of distorted trigonal bipyramids interconnected by shared edges and corners parallel to the (ab) layers.⁸⁴⁻⁸⁵ The room-temperature Raman spectrum (**Figure 3.2b**) of a V_2O_5 sample exhibits bands at 143, 198, 286, 306, 406, 483, 526, 702, and 996 cm^{-1} , which are

characteristic modes for this compound⁸⁶⁻⁸⁷. High-frequency Raman peaks at 996 cm⁻¹ and 702 cm⁻¹ correspond to the stretching modes of the V=O (terminal oxygen) and V₂-O (doubly coordinated oxygen) bonds respectively. The peak at 526 cm⁻¹ is assigned to the V₃-O (triply coordinated oxygen) stretching mode. The peaks located at 406 and 286 cm⁻¹ are assigned to the bending vibration of the V=O bonds; while those at 483 and 306 cm⁻¹ are assigned to the bending vibrations of V-O-V (bridging doubly coordinated oxygen) and V₃-O (triply coordinated oxygen) bonds, respectively. Transmission electron microscope (TEM) images (**Figure 3.2c**) reveal the morphology of the nanostructure. The top inset shows the corresponding selected area electron diffraction (SAED) pattern, confirming the growth of single-crystalline V₂O₅ in the [011] direction. Here, the brightest central spot in SAED is blocked in order to get a better contrast. The lattice-resolved image (**Figure 3.2d**) of a typical nanoribbon reveals the single-crystalline nature of the sample. An amorphous layer can be founded at the surface of nanoribbon. This layer could be formed during the cooling-down process after growth with the thickness varying along the nanoribbon and between samples.

3.2.2 Micro-optical Properties of the Individual Nanoribbon

A 457 nm laser was used to study the waveguiding properties of the as-grown V₂O₅ nanoribbons. **Figure 3.1b** shows an optical microscopy image of the samples with a notch-filter. Only part of the nanoribbon is shown in this figure because of the limited imaging area of the CCD. Significantly, the emission of the sample under laser

excitation was so strong that it could be imaged easily with a color CCD camera (768 pixel $\times$ 576 pixels). The large bright facula in the bottom right-hand corner of the image is the in-situ photoluminescence (PL) under laser illumination. Notable bright luminescence spots were observed at the end of the nanoribbon irrespective of the position of excitation on the sample, which is due to the waveguided PL emission scattering at the tip. The localization of the out-coupling of the light at the ends of each wire is a typical feature of the strong optical waveguiding behavior. In contrast, the body of sample is not visible in the optical image, showing that the V_2O_5 nanoribbons are promising low-loss components for photonic devices in the micrometer or nanometer scale. The effective waveguide behavior is attributed to the large difference between the refractive index of the nanostructure ($n_{V_2O_5} = 2.3$)⁸⁸ and those of the external media ($n_{air} = 1$ and $n_{SiO_2} = 1.45$), which results in tight optical confinement in the ribbons.

The dependence of the intensity of out-coupled luminescence at the rightmost tip of an unoptimized nanoribbon (width: ~ 320 nm, length: ~ 100 μ m) on propagation length is shown in **Figure 3.3a**. Considering the small fluctuations in excitation power, the measured intensities at the end-faces are normalized against those measured at each excitation location on the nanoribbon body. These data (**Figure 3.3b**) can be well-fitted by a first-order exponential decay function expressed by

$$I_{tip} / I_0 = \exp(-\alpha x), \quad (3-1)$$

where I_{tip} is the luminescent intensity measured at the tip, I_0 is the normalized intensity at the excitation spot, x is the propagation length and α is a fitting parameter.

The propagation loss is about 0.06 dB / μ m, which is much lower than the optical loss

of other subwavelength-structures such as metallic plasmon waveguides (~ 1 dB / μm)⁸⁹⁻⁹⁰ and organic nanowires (0.3 dB / μm)⁹¹. The effective waveguiding properties can be attributed to the good crystalline quality. However, the optical loss is still larger than the reports in ref. 65 and 69. Some sources for the propagation losses will be discussed later.

Figure 3.3 a) PL images of a single nanoribbon. PL images were collected upon excitation of the identical fiber at different positions. b) Normalized dependence of the tip out-coupled emission intensity on excitation location. The line is an exponential fit to the data yielding the loss coefficient for the waveguide.

To obtain further insight to the light propagation behaviour of the sample, the V_2O_5 nanoribbons were transferred onto a cover glass substrate (thickness: 0.17 mm), and the PL spectra of the emitted light with respect to the distance between the excitation point and the end of nanoribbon were investigated with a WITEC CRM200 Raman system. The setup is shown in **Figure 3.4a**. The excitation laser ($\lambda=457$ nm or 532 nm) was focused onto the sample using a $100\times$ optical lens ($\text{NA}=0.95$). The laser spot size was around 500 nm in diameter. The piezostage movement and data acquisition

were controlled using ScanCtrl Spectroscopy Plus software from WITec GmbH, Germany. The detected light was captured from the opposite side of the substrate with a 60 $\times$ cover-glass-corrected objective lens (NA=0.80), which can be motorized in three dimensions. The collected signals were routed to a TE-cooled charge-coupled-device (CCD) cooled to -64°C. With this technique, the procession of light traveling along the fiber can be effectively studied by moving the stage and collection lens. The absorption spectrum of the sample was acquired using a Varian Cary 100 UV-Vis spectrophotometer. All the measurements were taken at room temperature.

Figure 3.4b displays the spectra of the waveguided emission that is out-coupled at the tip as a function of increasing propagation length. The nanoribbon exhibits room-temperature luminescence in the 550–750 nm region, with a full-width at half-maximum (FWHM) of approximately 96 nm. This broad PL spectrum may help in manipulating light in the waveguides.^{70,80} As shown in **Figure 3.4b**, the intensity of the long-wavelength side of the PL decreases significantly with an increase in the guided distance, which results in a continuous blue-shift of the spectra. The absorption measurements (in **Figure 3.4b**) allow us to infer two important points about the sample. First, considering the band gap (~ 2.3 eV) of V₂O₅, the above-mentioned visible light emissions, obviously, should not be re-absorbed by interband transition along the fiber. Light with longer wavelength tends to suffer higher evanescent leakage, due to the decrease in optical confinement with increasing free-space wavelength λ .⁹² Second, a small absorption tail can be observed at about

700 nm. This low-energy absorption is associated with transitions involving impurity states within the energy gap, i.e. V^{4+} ions.⁹³ Such kind of native-defects levels are probably related to the absorption in the long-wavelength range. Overall, our data indicate that nanoribbons can be made into reasonably good short-pass filters with tuneable cutoffs based on path length, by exploiting evanescent leakage and impurity-state absorption.⁶⁸ Besides, we note that other experiment parameters such as light polarization, wavelength and fiber diameter, also affect the performance of these nanoribbons for such functions, which need further study.

Figure 3.4 Measurement of the waveguide characteristics of the nanoribbons. a) Schematic illustration of the experimental setup. b) Absorption and waveguided PL spectra of a V_2O_5 nanoribbon. The waveguided PL was captured at various excitation/tip distances.

The light coupling between two physically connected nanoribbons was also observed.

As shown in **Figure 3.5**, the laser was focused at one of the three ends of the connected nanoribbons, bright spot can be observed at the other two ends. In this way, light can be guided efficiently through sub-wavelength turns defined by junctions between two ribbons. Actually, it can be seen that the coupling efficiency could be

modified by the deviation angle of the coupling nanoribbon from propagation along a straight path of the coupled one.

Figure 3.5 Light coupling between two nanoribbons. The green circles show the locations where the laser was focused on. The physical connection between two nanoribbons was confirmed by SEM as inset.

The size dependence of the waveguide mode dispersion is crucial for understanding the fundamental size effects of strong optical confinement and the optimal design of nanowire-based photonic devices. Micro-PL from body of several uniform nanoribbons is shown in **Figure 3.6**. Taking into account the radial resonance, light could interfere with itself to enforce constructive interference, such as whispering

gallery modes (WGM)⁹⁴⁻⁹⁵. This kind of phenomena is very obvious at the body of nanostructures. It can be seen that the geometrical structure and size of nanoribbon can be used as a cavity to modify the photoluminescence properties. The nanoribbons can serve as a cavity and trap light by total internal reflection. As a result, high intensities can build up inside the nanoribbon when the light wavelength matches one of the optical resonances supported by the nanostructure. At these resonances, light can also be strongly scattered by the nanoribbon as some of the stored energy is returned to the far-field detector. The efficient coupling of light into and out of the nanoribbons reflects the leaky nature of the resonant optical modes of the nanostructures.⁹⁶

In contrast, the tips of nanoribbon act as the ends of Fabry-Perot cavity. So the spectra obtained from the tip are expected to show different kinds of profile. As shown in **Figure 3.7**, the emission spectrum obtained from the nanoribbon end shows pronounced modulation over a wide spectral range. The expected resonance longitudinal mode spacing is given by

$$\Delta\lambda = \frac{\lambda^2}{2L(n - \lambda \frac{dn}{d\lambda})}. \quad (3-2)$$

To investigate the mode competition in the waveguiding nanoribbons, a typical photoluminescence figure is shown in **Figure 3.7b**. The sharp peaks around ~550nm are caused by Raman phonons. The modulation at longer wavelengths is attributed to Fabry-Perot interference along the length of the ribbon. Here, we found some jumps in peakspacing and peak splitting on the interference peaks, which means the *multiple*

Figure 3.6 Photoluminescent properties on different samples.

modes (this is acceptable considering the large cross section) that we are detecting.

In addition to the above-mentioned nanoscale active optical waveguides, we were also interested in exciting Raman active modes in the waveguides by launching 457 nm light down the V_2O_5 cavities (i.e., near resonance Raman scattering⁹⁷⁻¹⁰¹). The light undergoes Raman scattering from molecules in the material, and this is expected to give rise to the Stokes shifted lines at longer wavelengths. **Figure 3.8** shows that

the peak positions detected at the tip (B) correspond well to the Raman spectra collected at the excitation point (A), accompanying the PL band of V_2O_5 . No significant broadening was observed in the Raman signal. The fluorescence spectrum from the body (C) was also observed, which was ascribed to some inevitable surface contaminants. These contaminants may scatter the guided light which results in a lower waveguiding efficiency. More importantly, we found that certain Raman signals collected at the tip, especially the peaks at around 550 and 1000 cm^{-1} , become dominant due to the transfer of energy from near-resonant excitation to those at longer wavelengths, and thus amplify the Raman signals. In fact, the Raman Stokes power is comparable to the broadband emission of the sample.

By fixing the collection point (tip), using Renishaw inVia Raman system, we could compare the in-situ tip Raman emission and waveguiding Raman outcoupling signal.

As shown in **Figure 3.9**, a very similar phenomenon was found. This described Ram-

Figure 3.7 PL mapping on an individual nanoribbon and the corresponding normalized emission from body and tip.

Figure 3.8 a) Spatially resolved emission spectra recorded at different positions of a sample. The inset shows the locations of the collecting points, A: excitation point; B: tip of nanoribbon; C: body of the ribbon; D: background. b) The corresponding Raman signals from collection points A and B.

an-active effect in V_2O_5 nanoribbons is extremely important in optical fiber communication systems and as devices on their own. And the basic function demonstrated in this work might open up opportunities in Raman nanofiber

amplifier/laser and other compact analytical devices. Indeed, stimulated Raman scattering in Si waveguides and Raman amplifier integrated with an external fiber-based optical feedback have been demonstrated to yield optically pumped Raman lasing in Si.¹⁰²⁻¹⁰⁵

Figure 3.9 Remote-excitation Raman signals detected using Renishaw inVia Raman system.

3.3 Conclusion

In summary, we have reported the synthesis of single crystalline divanadium pentoxide nanoribbons using a simple thermal vapor deposition technique. Considering the smooth surface and high refractive index which give rise to the tight optical confinement, it is the first demonstration of efficient light propagation in V_2O_5

nanoribbons. The results provide useful information for the construction of future nanoscaled waveguide structures. Moreover, regular V_2O_5 waveguides were found to exhibit Raman signals with near-resonance excitation and guide these modes through the nanoribbon cavity. The initial results shown here provide experimental support for the development of novel nanophotonic elements.

Chapter 4 Raman Mapping Probing of Tip-induced Anomalous Polarization Behavior in V₂O₅ Waveguiding Nanoribbons

4.1 Background

One-dimensional (1D) nanostructure is expected to be a critical component in future optoelectronic devices and represents a unique system for exploring phenomena at the nanoscale.¹⁰⁶⁻¹⁰⁸ Recently, significant progress has shown that the optical properties of the 1D specimen exhibit strong polarization anisotropy, due to the dielectric constant mismatch between a nanowire and its surroundings.¹⁰⁹⁻¹¹² However, most of the work focuses only on the spectra from the body of nanowire, which assumed the nanowire as a circular dielectric cylinder of infinite length.^{111,113-114}

Figure 4.1 Boundary conditions at the interface between two dielectric media.¹¹⁵

On the interface between two different homogeneous dielectrics, boundary conditions (Figure 4.1) require the continuity of the parallel component of the electric field:

$$(\vec{E}_2 - \vec{E}_1) \times \hat{n} = 0, \quad (4-1)$$

and the continuity of the normal component of the electric induction:

$$(\vec{D}_2 - \vec{D}_1) \cdot \hat{n} = \sigma = 0. \quad (4-2)$$

If we introduce the electrostatic potential φ , by

$$\vec{E} = -\nabla \varphi. \quad (4-3)$$

So the boundary conditions become:

$$\varphi_1 = \varphi_2, \text{ and } \varepsilon_1 \frac{\partial \varphi_1}{\partial n} = \varepsilon_2 \frac{\partial \varphi_2}{\partial n}. \quad (4-4)$$

Now we consider the polarization of the electric field perpendicular to the long axis of a one-dimensional nanowire (**Figure 4.2**). The potential outside of the cylinder can be written as

Figure 4.2 Schematic representation of the polarized experiments on an individual nanowire.

$$\varphi_{out} = -\vec{E}_0 \cdot \vec{r} - A \cdot \frac{\vec{E}_0 \cdot \vec{r}}{r^2}. \quad (4-5)$$

Here, the first term is the potential of the external field, and the second term is the change in the potential due to the nanowire cylinder (cylindrical coordinates is used, and A is a constant). The potential inside of the nanowire is expressed as

$$\varphi_{in} = -B \vec{E}_0 \cdot \vec{r}, \quad (4-6)$$

where B is a constant. Considering the boundary condition at $r=R$, we can get the

coefficients A and B as:

$$A = \frac{\varepsilon_{out} - \varepsilon_{in}}{\varepsilon_{out} + \varepsilon_{in}} R^2, \text{ and } B = \frac{2\varepsilon_{out}}{\varepsilon_{in} + \varepsilon_{out}}. \quad (4-7)$$

Therefore, we can get the perpendicular electric field inside the nanowire:

$$E_{in\perp} = \frac{2\varepsilon_{out}}{\varepsilon_{in} + \varepsilon_{out}} E_{out\perp}. \quad (4-8)$$

In contrast, from Eq. 4-1 the parallel component of the electric field should satisfy:

$$E_{in\parallel} = E_{out\parallel}. \quad (4-9)$$

Based on Eqs. 4-8 and 4-9, it can be seen that the difference in the dielectric constants between the nanowire and its environment results in polarization-sensitive optical absorption and emission in the one-dimensional nanomaterial.

Nevertheless, nanowire tips have different boundary conditions from the body, thus are expected to affect the optical spectra. In this context, it is crucial to describe effects at the nanowire tips, which have been shown to play important roles in nanolasing resonators to confine photons and tip-enhanced Raman scattering (TERS), etc.¹¹⁶⁻¹²² Therefore, spatially resolved imaging of a single nanostructure, which can provide detailed information on the localized area of interest, is particularly significant. Micro-confocal polarized Raman mapping is a useful technique for probing the physical properties of individual nanostructures in the rapidly evolving area of nanoscience with a reasonable spatial resolution.¹²³⁻¹²⁶ In this chapter, we report the use of polarized Raman imaging technique as a local characterization tool of an individual V₂O₅ nanoribbon. The exquisite spatial sensitivity allows for the

distinction between different optical properties at the ends and body of the sample. It is found that the natural dependence of Raman tensors and the strong polarized local field can lead to two distinct types of Raman-antenna patterns at the body and tips of one-dimensioned nanostructures.

4.2 Experimental Details

4.2.1 Preparation and Characterization of Samples

As we mentioned in **Chapter 3**, the V_2O_5 nanoribbons were grown by a thermal deposition method. A clean piece of vanadium foil (Lesker, 99.8 %) was heated at 660°C for four hours under ambient conditions. The nanoribbons were collected on Si or quartz substrates which were covered on the foil without the use of catalyst. A representative dark-field optical image of the as-grown samples is shown in **Figure 4.3a**. The selected-area electron diffraction (SAED) pattern in **Figure 4.3b** reveals that the ribbons have a single-crystalline structure and the growth direction is along [011]. Furthermore, high-resolution transmission electron microscope (HRTEM) images from different positions of sample demonstrate the uniformity along the nanoribbon. For optical studies, the nanoribbons were dispersed onto a glass substrate after being removed from their growth substrates by ultrasonic agitation in acetone. As shown in **Figure 4.3d**, the Raman spectrum of the sample corresponds well to the characteristic modes of crystalline V_2O_5 .¹²⁷ (The spectrum is taken from body of sample and no analyzer is used in this case.)

Figure 4.3 (a) Dark-field image of an as-grown sample. (b) TEM of a single crystalline nanoribbon. (c) Photoluminescence images of the nanoribbon show promising waveguiding properties. As highlighted by the green circles, the exciting laser spot was focused at the middle, right and left ends, respectively. (d) Typical Raman scattering spectrum of the sample.

Divanadium pentoxide (V_2O_5), which exhibits highly anisotropic electronic and optical properties, can be an outstanding candidate for optoelectronic applications.

The active waveguide properties on the V_2O_5 nanoribbons have been studied in our previous work.¹⁰⁸ An example of this waveguiding is shown in **Figure 4.3c**, where a V_2O_5 nanoribbon was excited by a 532 nm laser focused at the middle, right and left ends of the sample. It can be seen that the light travels along the ribbon and emerges

at the ends. In addition, we found that the Raman signals also exhibit pronounced waveguide effect, suggesting that these nanostructures may be potentially useful for novel sub-wavelength optoelectronic devices.

Figure 4.4 Experimental setup for polarized Raman experiments on individual nanoribbons.

Polarization-dependent Raman measurements on individual V_2O_5 nanoribbons were investigated in backscattered configuration by WITEC CRM200 confocal system, together with a high-resolution piezoelectric stage. A laser beam ($\lambda=532$ nm) was focused down with a $100\times$ ($N. A. =0.95$) objective. And the polarized Raman spectra

were acquired at room temperature by rotating a linear polarization analyzer in the collection optical path while excitation polarization was maintained. Nanoribbons were aligned to be parallel to the polarization of the incident laser (as shown in **Figure 4.4**). The *Porto notation* will be used to indicate the polarization configuration in which each spectrum was taken. For example, the symbol $Z(XY)\bar{Z}$ means that the laser light is incident from the Z direction with the X polarization, while the scattered signal is collected with the Y polarization in the opposite Z direction.

4.2.2 Results and Discussions

Polarized Raman images on individual nanoribbon, constructed by extracting integrated intensities of different phonon modes (A_g : 996 cm^{-1} ; B_{1g} : 702 cm^{-1} ; B_{2g} : 143 cm^{-1}), are shown in **Figure 4.5a** by recording the data with about 200 nm/pixel and an integration time of 0.5 s/pixel. In fact, all images generated using the same phonon modes, exhibit nearly identical patterns. Considering the polarization dependences, two distinct homogeneous contrast images of A_g modes for different polarization geometries demonstrate the high crystalline quality along the nanoribbon^{124,126}, which is also consistent with our TEM result. Meanwhile, one of the most dramatic phenomena is that, B_{1g} (B_{2g}) modes exhibit predominant emission at the tips in $Z(XX)\bar{Z}$ configuration in contrast to the uniform intensity distribution along the nanoribbon for $Z(XY)\bar{Z}$ geometry and show a strong polarization dependence. In other words, B_{1g} and B_{2g} can be notably enhanced at end facets of the nanoribbon in $Z(XX)\bar{Z}$ configuration. Actually, as shown in **Figure 4.5b**, no

obvious intensity change was observed on A_g modes, while pronounced B_{1g} and B_{2g} emission from the tips can be collected (which are labeled with arrows). Understanding of these results, in addition to providing insight into geometry-broken induced optical properties, will facilitate the rational design of Raman detection in nanostructures.

Figure 4.5 (a) Raman images of the nanoribbon constructed by extracting the integrated intensities of the different modes for $Z(XX)\bar{Z}$ and $Z(XY)\bar{Z}$ polarization configurations: A_g (996 cm^{-1}), B_{1g} (702 cm^{-1}) and B_{2g} (143 cm^{-1}).

The scale bar is 5 μm . (b) Raman scattering signals at the body and tip of sample under $Z(XX)\bar{Z}$ configuration.

To further explore the origin of the phenomenon described above, we have compared the angular dependence of the Raman emission from body and tip of the V_2O_5 nanoribbon which shows striking differences. Note that the unique rectangular cross-section provides the complete orientation of the crystal axes relative to the plane of the substrate (**Figure 4.6**). So the polarization dependence of different phonon modes can be predicted accurately based on the Raman tensor analysis.

Figure 4.6 We can get the complete orientation of nanoribbon, especially the direction relative to the plane of substrate.

According to the group-theoretical treatment, the Raman tensors ($\vec{R}$) of V_2O_5 with orthorhombic symmetry D_{2h} are as follows:

$$\vec{R}(A_g) = \begin{pmatrix} a & & \\ & b & \\ & & c \end{pmatrix}, \quad \vec{R}(B_{1g}) = \begin{pmatrix} & d & \\ d & & \\ & & \end{pmatrix}, \quad \vec{R}(B_{2g}) = \begin{pmatrix} & & e \\ & & \\ e & & \end{pmatrix}$$

where a , b , c , d , and e are components of the Raman tensors.¹²⁸ The observed Raman scattering intensity is given by $S = A \left| \hat{e}_s \cdot \vec{R} \cdot \hat{e}_l \right|^2$, where A is the constant and $\hat{e}_{l,s}$ represents unit vectors of the incident (l) and scattered (s) light, respectively. In the mentioned backscattering configuration, the incoming and scattered vectors are given by

$$\hat{e}_l = \begin{pmatrix} 0 \\ \cos \varphi \\ \sin \varphi \end{pmatrix} \text{ and } \hat{e}_s = (\cos \varphi \sin \theta \quad \cos \varphi \cos \theta \quad \sin \varphi)$$

where θ is the angle between a primary axis such as $\langle 011 \rangle$ direction and the radiated electric field, and φ is the cross angle between $\langle 010 \rangle$ and $\langle 011 \rangle$ directions in the (100) plane. So the Raman intensity as a function of θ will be given by

$$S(A_g) \propto \cos^2 \theta, \quad S(B_{1g}) \propto \sin^2 \theta, \quad S(B_{2g}) \propto \sin^2 \theta.$$

As shown in **Figure 4.7a**, the polarization dependent intensities from the body of nanoribbon are, in general, consistent with the Raman tensor analysis. Therefore, the antenna effects on the body of nanoribbon should have nothing to do with the phonon confinement. All the A_g modes have the maximum at $\theta = 0^\circ$, which corresponds to the $Z(XX)\bar{Z}$ configuration, while both B_{1g} and B_{2g} modes follow the square of sine function and with a maximum at $\theta = 90^\circ$, equivalent to the $Z(XY)\bar{Z}$ configuration. This feature was further confirmed by the polarized Raman spectra from the body of sample (**Figure 4.8a**), which shows a strong anisotropic behavior. The Raman intensity is normalized to the maximum intensity. Also, the relative intensity for B_{1g} (B_{2g}) modes in $Z(XY)\bar{Z}$ configuration became predominant compared to that in $Z(XX)\bar{Z}$ configuration. In contrast, when we focus the laser at the tips of nanoribbons, the spectra under different experimental setup exhibit similar line shapes as shown in **Figure 4.8b**. Furthermore, we surprisingly found that in our case all the phonon modes detected at the tip exhibit the same dipole-antenna polarization behavior which can be well-described by a $\cos^2 \theta$ function (**Figure 4.7b**). Actually,

in $Z(X\bar{X})\bar{Z}$ configuration ($\theta = 0^\circ$, corresponding to the nanoribbon axis parallel to the direction of the analyzer) the B_{1g} and B_{2g} modes are suppressed at the body of sample while enhanced at the ends. Meanwhile, A_g modes do not show much suppression either at the tip or body of nanoribbon. Thus, we can expect that the appearance of the bright spots at both tips for B_{1g} - and B_{2g} -mode peaks, while homogenous spatial distribution of the A_g emission along the ribbon (as shown in Figure 4.5).

Figure 4.7 Polar plots for A_g (996 cm^{-1}), B_{1g} (702 cm^{-1}) and B_{2g} (143 cm^{-1}) scattering intensities versus polarization angle θ , from the body (a) and tip (b) of the nanoribbon, respectively.

The polarization anisotropy is very useful for the selective detection of certain phonons. Fréchette and Carraro have reported¹²⁹ that the large suppression of the depolarized signal provides an opportunity to increase the sensitivity of Raman scattering from surface modes relative to bulk modes. In our case, the results show that the sensitivity of Raman modes could also be changed due to the local positions. At the tip of nanoribbon, a different boundary condition could be expected compared to the middle portion. Recently, Poborchii¹³⁰ also reported that the edge brings about a strong electric field with a resultant Raman signal enhancement. Combined with the anisotropy of the dielectric susceptibility tensor, the different electric field components could result into a change of in/out-coupling efficiency. The local electric field intensities along the nanoribbon were simulated by finite element method (FEM), as shown in **Figure 4.8d**. Light (532 nm) was taken to be incident normal to the nanoribbon axis and electric field was parallel to the nanoribbon axis (transverse magnetic polarization). It can be seen that the calculated electric field intensity has “hotspots” at the tips of the nanoribbon. Under these circumstances, it is conceivable that the outcoupling is strongly enhanced at the tips of sample, which would be directly related to the direction of the polarization of the scattered light.^{114,131} Hence, the suppressed phonon signals at the body of a ribbon intensifying at the end facets could be expected. The results also indicate the potential applications for polarized tip-emission light source.¹³²⁻¹³³

Figure 4.8 Comparison of the normalized polarized Raman spectra parallel ($Z(XX)\bar{Z}$) and orthogonal ($Z(XY)\bar{Z}$) to the nanoribbon axis collected at the body (a) and tip (b) of sample. (c) Waveguided Raman spectra out-coupled at the tip of nanoribbon under parallel ($Z(XX)Z$) and perpendicular ($Z(XY)Z$) polarized collection conditions, respectively. (d) The simulated field distribution of a V_2O_5 nanoribbon.

In addition, the squared cosine dependence (as shown in **Figure 4.7b**) can be rationalized by considering the effective waveguiding propagation along the nanoribbon of the nanostructure and the strong local intensity at the end of the nanostructures.^{121,130,134} The propagation of Raman signals along V_2O_5 nanoribbon has

been reported in **Chapter 3**.¹⁰⁸ In the present case, the suppressed Raman signals can be guided along the nanoribbon to exit at the tip and result into a strong polarized outcoupling emission (enhanced parallel to the nanoribbon axis and suppressed perpendicular to the nanoribbon axis). To demonstrate the optical propagation effect in V_2O_5 nanoribbons, we have explored the spectral variation of polarized Raman-active waveguide emission using a WITEC CRM200 Raman system.

Figure 4.9 Measurement of the waveguide characteristics of the nanoribbons. The excitation laser was focused onto the body at about $10\ \mu\text{m}$ distance away from the tip of sample. The waveguided signals were captured at the tip of nanoribbon from the opposite side of excitation. An analyzer was inserted into the collection path. In this regard, the polarized properties of waveguided photons can be investigated (**Figure**

4.9). It is apparent from the spectra shown in **Figure 4.8c** that intensities of all the Raman modes were significantly decreased when the collection polarizer was oriented perpendicular to the long axis of the nanoribbon, consistent with the polar plots in **Figure 4.7b**. Several nanoribbons with different cross-sections were also tested. By the detailed analysis of the polarization dependence of the emission, the waveguide-assisted nature of the Raman scattering can be proven.

4.3 Conclusion

In summary, this work demonstrates remarkable effects of nanoribbon ends in Raman scattering. We have studied the polarized Raman properties of V_2O_5 using confocal microscopy. Detailed polarized optical properties analysis indicated that the polar scattering patterns are mainly governed by bulk Raman tensors at the body. While at the tip of the sample, the effective waveguides and tip-enhanced outcoupling would be directly related to the direction of phonon scattering. This gives rise to a pronounced Raman intensity contrast along the sample for certain configuration. The anomalous behavior is expected to be a general effect in other one-dimension nanostructures and demonstrates prospects of the tip effect on optoelectronic nanodevices.

Chapter 5 Orientation Controllable Growth of MoO₃ Nanoflakes: Micro-Raman, Field Emission and Birefringence Properties

5.1 Introduction

Effect of dimensionality and geometry on nanomaterials has been extensively studied to meet the demands of miniaturization and better performance for applications. To date, however, controlling the orientation of nanostructure is still a challenge. Recently, substrates with specific crystallographic orientations but having good lattice matching to the nanowires (NWs) were chosen to induce the NWs growth along different orientations.¹³⁵⁻¹³⁷ In addition, due to the anisotropic properties of samples, various of novel physical properties can be expected.^{40,138-140} Here we demonstrate a simple but effective way to manipulate the as-grown orthorhombic molybdenum trioxide (α -MoO₃) nanoflakes. Compared with nanowires, nanoflakes have well defined crystallographic surfaces, which offer opportunities to investigate the anisotropic parameters on nanomaterials.

The crystalline structure of MoO₃ can be visualized as corner-sharing chains of MoO₆ octahedrons that share edges with two similar chains to form layers of MoO₃ stoichiometry in the *ac*-plane (inset of **Figure 5.1a**). The layers are stacked in a staggered arrangement along the *b* axis direction and are held together by van der

Waals' forces. As one of most important layered oxides, combined with the unique ability of transition-metal ions to change easily their oxidation state and/or arrangement of the coordination polyhedra,¹⁴¹ it is a good candidate for applications as catalyst¹⁴², sensor¹⁴³, field emission¹⁴⁴, photo- and electro- chromic devices¹⁴⁵.

5.2 Experimental Methods

In this contribution, the MoO₃ nanoflakes were fabricated by modified hotplate method.¹⁴⁶⁻¹⁴⁷ A Mo foil (15mm×15mm×0.2mm) with a purity of 99.9% (Aldrich) was used as the heating target. After being carefully cleaned, it was loaded on the hotplate. A piece of gold-coated-Si (Sample 1) or Si (Sample 2) was used as the deposition substrate and laid above the foil with a 0.7 mm distance between the foil and substrate surface.³⁷ Crystalline α -MoO₃ nanoflakes were observed on the silicon substrate after the foil was heated to 450 °C for 4 hours. Structural details of the nanoflakes were characterized by X-ray diffraction (XRD) (Bruker D8 with Cu K _{α} irradiation). The observation of the morphology of the samples was carried out using a JEOL JSM-6700F field-emission scanning electron microscope (FESEM). Transmission electron microscopy (TEM) was performed using a 200kV field-emission-gun (JEOL 2010F).

The polarized micro-Raman spectra from individual nanoflakes were carried out with a WITEC CRM200 confocal Raman system using backscattering configuration, where the incident and scattered unit polarization vectors can be mutually rotated in the horizontal microscope plane. Field emission measurements were recorded using

parallel-plate configuration in a high vacuum chamber with a pressure of 3.8×10^{-7} Torr at room temperature. The nanostructure film is firstly mounted onto a steel plate as the cathode. Indium-tin oxide (ITO) glass is used as the anode to collect field emitted electrons. A Polyethylene terephthalate (PET) transparency film, with a thickness of 100 μm and a hollow of 0.04 cm^2 , is utilized to be the spacer. So that the gap between electrodes and area of sample are defined.¹⁴⁸ A Keithley 248 high-voltage source unit was used for sourcing the voltage and a Keithely 237 for measuring the current.

Optical polarization microscopy was performed on an Olympus BX 51 microscope equipped with both a polarizer, positioned in the light path before the specimen, and an analyzer, placed in the optical pathway between the objective rear aperture and the observation camera port. In this case, the birefringence properties can be investigated by rotating the specimen stage.

5.3 Results and Discussions

5.3.1 Characterization and Growth Mechanism

The XRD patterns of the samples are shown in **Figure 5.1a**. All of the reflection peaks can be indexed to $\alpha\text{-MoO}_3$. **Figure 5.1b** shows the TEM image of an individual as-grown nanoflake. The amorphous layer can be found on the surface of nanostructure, which might be attributed to the sudden termination of feeding vapor as the evaporation was ceased. The selected area electron diffraction (SAED) pattern of the nanostructure is displayed in the inset of **Figure 5.1b**, revealing

well-crystallized single crystals. Considering the crystalline structure of MoO_3 , we can see that the thickness of lamella should be mainly along $\langle 0k0 \rangle$ direction, which gives rise to a relatively intense diffraction peak of $(0k0)$ plane as shown in **Figure 5.1a**. The absence of redundant XRD peaks in sample 2 indicates excellent overall b -axis alignment of these nanoflakes over a large substrate area (the nanoflakes are mainly laid on the substrate). While the appearance of (110) and (021) peaks elucidate the vertically standing of sample 1, which can be further confirmed by SEM images.

Figure 5.1 (a) XRD of the as-grown samples. Inset: structural model of MoO_3 with layered structure. (b) TEM image of the MoO_3 nanoflakes and the corresponding electron diffraction patterns.

As shown in **Figure 5.2**, the wire-like features were produced from the top-view of sample 1, which is due to the nanoflakes aligned in a highly dense array approximately perpendicular to the substrate surface. The coverage of the array on the substrate appears to be quite uniform judging from the SEM images. Cross-section SEM measurements also show that these flakes grow vertically to the substrate surface. While for sample 2, the nanoflakes are just parallel to the substrate. These observations point to the importance of gold in mediating the growth of MoO_3 nanoflakes.

The growth of molybdenum trioxide lying on the substrate (sample 2) has been demonstrated previously by vapor-solid (VS) mechanism.¹⁴⁹ To explain the preferable vertical growth of sample 1, high-resolution SEM images are shown in **Figure 5.2e, f** and **g**. It is observed that Au particles emerge with nanoflakes at the bottom instead of on the top the structures, even at the very beginning period of growth (**Figure 5.2g**), which is reminiscent that the growth of vertical nanoflake is still governed by VS mechanism.

Figure 5.2 SEM images of sample 1 and 2: (a), (c) top view; (b), (d) cross-section. High-resolution SEM of sample 1: top edge (e) and bottom (f) of the erected MoO_3 nanoflake. (g) SEM image of sample 1 after being heated for 10 minutes.

It is likely that the gold particle strongly lowers the barrier for the incorporation of vapor at the substrate, thus making nanoflakes grow erectly.¹⁵⁰ Besides, the interaction of Au with oxygen facilitates the diffusion of incoming vapor, which will influence the orientation of the seeds¹⁵¹⁻¹⁵² and result into the change in arrangement of nanoflakes. From these arguments, it is reasonable to expect that the orientation of single-crystalline MoO₃ nanoflakes can be modified in the presence of Au particles. To further confirm the VS processes, the length and width of more than 50 nanoflakes were measured. As known, the Vapor-Liquid-Solid (VLS) growth tends to produce nanostructures with higher length-to-width ratios than the VS process.¹⁵³ The scattered dates (not shown here) indicate an average length-to-width ratio of about 3.25. The value doesn't change significantly for both samples, which also indicates the same VS growth mechanism.

5.3.2 Micro-Raman Properties

The unique orientation-ordered geometry of MoO₃ nanoflakes provides a chance to study the physical properties on different crystal faces. Polarized micro-Raman spectra of samples 1 and 2 are presented in **Figure 5.3** under four different scattering configurations. The *Porto notation* was used to indicate the scattering setup in which each spectrum was taken. For example, the symbol $Z(XY)\bar{Z}$ represents that the laser light is incident from the Z direction with the X polarization, while the scattered signal is collected with the Y polarization in the opposite Z direction. The positions of all the Raman peaks observed are in good agreement with those described in the

literature,^{99,154-155} while the intensity of the vibration modes varies based on the crystal orientation and the polarized configurations. The observation also confirmed the single-crystalline structure of the samples.¹⁵⁶

Figure 5.3 Polarized-Raman spectra of sample 1 (a) and sample 2 (c). The enlarged spectra in $Z(XY)\bar{Z}$ configuration with curve fitting are also shown in panels (b) and (d).

The Raman peak at 996 cm^{-1} can be assigned to the asymmetric $\text{Mo}=\text{O}_1$ stretching along the b -axis direction, while the peak at 819 cm^{-1} is coming from the symmetric $\text{Mo}-\text{O}_3-\text{Mo}$ stretching with the bonding aligning along the a -axis.¹⁵⁴ It is observed that the peak strength at 996 cm^{-1} of sample 1 is stronger than sample 2. For the as-grown sample 1 (side edge of MoO_3 nanoflake), b -axis direction is perpendicular to the direction of the optical path, which will increase the scattering cross-section, especially under $Z(YX)\bar{Z}$ configuration. In contrast, a -axis of sample 2 is parallel to the propagation direction. For the same reason, the signal at 819 cm^{-1} becomes

dominating in sample 2. These anisotropic spectra can be used as a benchmark for simple and rapid measurements of nanoflake orientations.

Figure 5.4 Raman intensity image of the nanoflake constructed by I_{284} (a), I_{293} (b) and I_{293}/I_{284} (c).

Moreover, the two wagging modes of the terminal Mo=O₁ groups at 284 cm⁻¹ (B_{2g}) and 293 cm⁻¹ (B_{3g}) are shown in **Figure 5.3b** and **d**. For sample 1, the B_{3g} mode is about two times stronger than B_{2g} mode. But in the spectra collected from (010) crystalline face (**Figure 5.3d**), the B_{3g} mode has only one-seventh of the intensity of B_{2g} mode. Actually, these wagging modes are both polarized parallel to the *c*-direction, and hence, the changing of intensity ratio reflects symmetry breaking introduced by the oxygen defects.^{99,157} Far-field Raman mapping was also utilized to further confirm the defects distribution of individual nanoflakes (no analyzer is used in this case). As shown in **Figure 5.4a**, the intensity of B_{2g} (centered at 284 cm⁻¹) is uniform over the entire (010) surface plane. In contrast, the B_{3g} band (centered at 293 cm⁻¹), as shown in **Figure 5.4b**, exhibits significantly enhancement at the edges of nanoflake. Similarly, the ratio image of I_{293}/I_{284} (**Figure 5.4c**) demonstrates clearly that the oxygen defects tend to be at the edge of the lamella. As known, the higher degree of oxygen defects will induce different metal oxidation states, which can promote the catalytic activities. This detailed detection about the distribution of vacancies on different crystalline facets will be helpful for a rational design of more efficient and selective catalysts.

5.3.3 Electrical and Micro-optical Properties

In this work, field emission properties of samples are also investigated. The typical current density–electric field (*J*–*E*) curve of sample 1 is depicted in **Figure 5.5**. The turn-on voltage is about 11 V / μm, which is defined as the field to produce a current

of $10 \mu A/cm^2$ for typical operation in flat-panel display. But for sample 2, we found it is *difficult to turn on* the field-induced emission. Using the Fowler-Nordheim (FN) equation for the field emission:

$$J = A \left(\frac{\beta^2 E^2}{\phi} \right) \exp(-B\phi^{3/2} / \beta E), \quad (5-1)$$

where $A=1.56 \times 10^{-10}$ (A V⁻²eV), $B=6.83 \times 10^9$ (V eV^{-3/2} m⁻¹), ϕ is the work function, and β denotes the field enhancement factor, which is related to the emitter geometry, its crystal structure, and spatial distribution of the emitting centers.

Figure 5.5 Field emission current-voltage characteristics of sample 1. The inset shows Fowler-Nordheim (F-N) plot.

Based on the equation (5-1), when $\ln(J/E^2)$ is plotted versus $1/E$, one obtains a straight line with a slope that depends on the work function of material and on the field enhancement factor β (as shown in the inset of **Figure 5.5**). The value of β was obtained to be about 2500, which is also about 4 times larger than the report showing

a more random-arrangement¹⁵⁸ and comparable to some other II-VI nanomaterials¹⁵⁹⁻¹⁶¹.

The larger field enhancement factor can be ascribed to the sharp edges of erected nanoflakes. In addition, the oxygen vacancy-type defects may play a critical role in defining the surface properties of the sample.¹⁶²⁻¹⁶³ The modification of surface electronic structure usually alters the Fermi level (work function), and we propose that the oxygen vacancies can reduce work function¹⁶² of the side edges of nanoflakes, which facilitates the electron emission process. As an n-type semiconductor, the oxygen vacancies in MoO₃ act as electron donors. So these donors could shift the Fermi energy level up, and consequently, the work function (which is defined by the energy difference between Fermi energy level and vacuum level¹⁶⁴) is lowered. Besides, the removal of the originally negatively charged oxygen ions might lead to the reduction of the Mo ions. It is proposed that the higher concentration of Mo^{δ+} (δ<6) species result into a decrease in work function, which is similar to ref. 31. Further work on UPS and XPS can be expected. The results also indicate anisotropic crystal structure and orientation can affect the performance of nanostructures.

Furthermore, to elucidate the anisotropic optical properties of α-MoO₃, the nanoflakes are deposited onto a glass substrate and *firstly* observed under a polarizing optical microscope using orthogonal linear polarization mode. When drop-cast on substrates from dispersions, the nanoflakes tend to rest on their wide axis. **Figure 5.6a** depicts two nanoflakes placed nearly at right angles to each other. The different colors are attributed to the optical interference. Polarized light image of the samples with

different rotation angles are illustrated in **Figure 5.6b-g**, which shows obvious birefringence due to its anisotropic crystal structure.¹⁶⁵⁻¹⁶⁷ When the incident light is polarized parallel to only one optical axis, the material appears dark under crossed polarizers, which correspond to the position of extinction. As the sample rotates away from the position of extinction, splitting of the beam occurs, and the sample appears in the microscope. The nanoflakes are brightest when their spatial axes are about 45° from the polarization angle. Therefore, the contrast between these two nanoflakes can be modified as we rotate the sample. The strong birefringence is attributed to the refractive indices varies with different crystallographic axes ($n_a=2.29$, $n_b=1.88$, $n_c=2.54$)¹⁶⁸ which is constrained by the point group symmetry of the crystal ($Pbnm-D_{2h}^{16}$). This distinct phenomena reported here makes MoO₃ nanoflakes effective building blocks to control the polarization of light in future miniaturized photonics. A more accurate measure of the birefringence can also be expected.

Figure 5.6 (a) Photomicrograph of samples in normal reflected light. (b-g) Samples observed through cross-polarized optical microscopy with different rotation angles. Scale bar is 5 μm . The top right schemes depict the crossed polarizers (double white arrows).

5.4 Conclusion

We demonstrate a simple but effective way to control the orientational arrangement of MoO_3 nanoflakes, which offers an opportunity to investigate the anisotropic properties of different crystallographic faces. Micro-Raman spectra of the samples revealed that oxygen vacancies prefer to concentrate at the side edges of the lamella. Combined with the unique structural geometry, the oxygen-defects induced reduction of work function on the sharp edges enables the erected MoO_3 nanoflakes to show promising field emission properties. In addition, strong birefringence properties of sample were firstly observed under the polarized light microscope due to their anisotropic crystal structure.

Chapter 6 Localized Suppression of Longitudinal-optical (LO) Phonon-exciton Coupling in Bent ZnO Nanowires

6.1 Introduction

Combined with the chemical stability, the high flexibility of metal-oxide nanowires enables them to be one of the most promising components for elastic optoelectronics.^{108,169-171} One of the important issues under intensive investigation is the bending effect, which is a typical deformation that occurs in the flexible devices¹⁷². In particular, Wang proposed that a lateral electrical potential can be achieved by bending the ZnO nanowire due to its piezoelectric property.¹⁷³ This kind of piezoelectric effect may influence the electrical transport characteristics of the nanowire-based field-effect transistor (FET).¹⁶⁹ In addition, tensile or compressive strains are expected to benefit from the bowing of nanowires, which could modulate the energy band structure¹⁷⁴⁻¹⁷⁵ and the carrier effective mass¹⁷⁶. However, relatively less effort has been devoted to optical properties of the curved ZnO nanowires¹⁷⁴, especially effects on the phonon-exciton interaction. Being a polar semiconductor, ZnO experiences a strong Fröhlich Interaction (FI) that gives rise to longitudinal optical (LO) phonon-exciton interaction. Herein, the coupling between exciton and phonon along the bent nanowire was investigated by confocal micro-photoluminescence spectroscopy.

6.2 Experimental Details and Discussions

6.2.1 Experimental Details

The ZnO nanowire samples used in this study were synthesized on silicon substrates by Au-catalyst-assisted chemical vapor deposition method in a horizontal tube furnace.¹⁷⁷ The large aspect ratio and elastic flexibility allowed manipulating the location and shape of individual nanowires under the optical microscope using a commercial micromanipulator tipped with sharp tungsten probes. The morphological and crystal structures were characterized by scanning electron microscopy (SEM) (JEOL JSM-6700F) and transmission electron microscopy (TEM) (200 kV JEOL 2010F). The temperature dependent PL measurement of the as-fabricated samples was performed between 10 and 300 K within a closed-cycle helium cryostat and a He–Cd laser (325nm) was used for excitation. The micro-photoluminescence and Raman spectra of individual nanowires were measured using the same laser line and a confocal Raman microscope (inVia Renishaw Raman) at room temperature. The spot size is about 1 μm with low excitation power density to avoid laser-induced heating effects in the sample.

6.2.2 Results and Discussions

Figure 6.1a shows the TEM images of the samples. The diameter of the ZnO nanowires is about 50 nm, with a smooth surface. The d -spacing of 0.26 nm from high resolution TEM (**Figure 6.1b**) corresponds to the lattice spacing of (0001) planes of

wurtzite ZnO. The dark lines on nanowire are thickness fringes due to the interference of electron beam.

Figure 6.1 (a) TEM images of the ZnO nanowires. (b) High-magnification TEM and the corresponding selected area electron diffraction (SAED) pattern.

At low temperature (10 K), the PL spectrum of the as-grown sample exhibits several peaks (as shown in **Figure 6.2a**), which correspond to the free exciton (FX) emission, the neutral-donor-bound exciton (D^0X) emission, and their LO-phonon replicas separated by a constant energy interval of 72 ± 2 meV. FX- n LO transitions are dominant than D^0X - n LO transitions, which indicates that the coupling of FX to the LO phonon is stronger than that between D^0X and LO phonons. Besides, up to fifth-order phonon replicas of free-exciton emission could be distinguished, showing the high crystalline quality and strong coupling of phonon and exciton in our ZnO nanowires. **Figure 6.2b** depicts the temperature-dependent PL spectra of the as-grown sample. As temperature increases, the intensities of D^0X -related emissions decrease much faster than that of FX and FX- n LO due to the thermal activation of the donor-bound exciton, and *finally FX and its first two replicas transitions are dominant at room temperature*. This strong coupling between FX and LO phonon provides a

possibility to investigate the bending effect on exciton-phonon interactions by deconvolution analysis of the spectra¹⁷⁸⁻¹⁸⁰, which will be discussed later.

Figure 6.2 (a) UV emission of the as-grown sample at 10 K. (b) Temperature-dependent photoluminescent properties of sample. The evolution of FX, D⁰X, FX-1LO and FX-2LO peaks are indicated by solid lines.

Micro-Raman technique is used to probe the local strain effect on an individual nanowire. A typical bent ZnO nanowire of 56 nm in diameter, 8 μm in length is shown in the inset of **Figure 6.3a**. The Raman spectra acquired at different positions are summarized using semi-logarithmic coordinates (**Figure 6.3a**). All spectra display two clear phonon modes which can be associated with the Si substrate Raman peak at 520 cm^{-1} and the LO phonon of ZnO. At the straight part of ZnO nanowire, the peak position of LO phonon mode is found at 579 cm^{-1} , close to the value expected for wurtzite ZnO¹⁸¹. At that position, the full width at half maximum (FWHM) is about 21.82 cm^{-1} . For the curved part of the nanowire, it displayed a significant shift of the phonon energy toward lower frequencies (574 cm^{-1}) with a FWHM of 22.58 cm^{-1} . As

known, the LO phonon in ZnO is very sensitive to the strain and formation of defects. Compressive and tensile stresses of the sample will shift the phonon peak to a higher and a lower wavenumber, respectively. The presence of structural defects is expected to broaden the Raman peaks. In this case, we can claim that, local tensile strain can be introduced by bending the nanowire without obvious crack defects and such a bending deformation is elastic.

Figure 6.3 (a) Normalized Raman spectra acquired at different position of the bent ZnO nanowire. (inset) SEM image of a strongly curved ZnO nanowire. (b) Deconvolution analysis for the corresponding PL spectra from straight and curved parts.

In an ideal case, the nanowire is expected to experience simultaneous compressive strain on the inner side of the curvature and tensile strain on the outer side, while the central area is free of strain. So the Raman peak at the bending part should be symmetrically broaden with no shift of peak position¹⁸². However, it is found the strain distribution is very dependent on the materials and different loading conditions. For example, for Ge, the compressive strength is expected to be an order of magnitude larger than the tensile strength.¹⁸³ Meanwhile, as we manipulated the nanowire on the silicon substrate, the surface force such as adhesion and friction forces¹⁸⁴ between

nanowires and substrate, could also influence the strain distribution. In our experiment, the LO Raman mode shifts toward lower wavenumbers, revealing the tensile stress at the curved part of ZnO under bending effect. So we proposed that the outer wall of nanowire would suffer more deformation than inner part, resulting tensile strain dominance. As the laser spot is large compared to the diameter of nanowire, the detailed mechanism of the bending induced tensile strain requires further study.

The tensile strain that we have observed experimentally from Raman scattering should result in some *local* effects on the electronic states and exciton-phonon interaction. Band gap shrinkage induced by tensile strain in ZnO has been realized recently¹⁷⁴. Of special interest in this study is the exciton-phonon coupling at the curved part of nanowire. The corresponding micro-photoluminescence spectra were collected as shown in **Figure 6.3b**. In order to quantify the relative contributions of the FX and its phonon replicas processes to the room-temperature PL, both spectra from straight and bent parts of the nanowire were well fitted by three Lorentzian peaks¹⁷⁸⁻¹⁸⁰, which determined to the contribution of FX, FX-1LO and FX-2LO (as discussed before). No obvious peak interval variability was observed for different positions. Generally, the emission intensity of the n th phonon replica I_n and the zero-phonon line I_0 is related by

$$I_n = \frac{S^n}{n!} I_0. \quad (6-1)$$

S is the so called Huang-Rhys factor, which provides a quantitative description of exciton-phonon coupling property. However, it was found that the ratio I_{FX-1LO}/I_{FX} can lead to erroneous conclusions about the Huang-Rhys factor, as the zero-phonon band

may consist of several decay sources¹⁸⁵⁻¹⁸⁶. Thus, we make a rough estimation of exciton-phonon coupling by the intensity ratio of FX-2LO to FX-1LO emission.

As shown in **Figure 6.3b**, the FX emission is suppressed compared to its first LO phonon replica for the *strongly* bent region. We tentatively ascribed it to the bending-induced defects or traps. Excitons can decay nonradiatively via defect states. In this case, the reduction of FX-1LO emission may be smaller than that of FX emission considering the fast relaxation time of the LO-phonon emission,¹⁸⁷ and defects can even increase/influence the relative intensity of 1LO-phonon scattering¹⁸⁸⁻¹⁸⁹. The significant suppression of FX emission compared to the FX-1LO emission can be associated with the dissociation of the exciton which might enhance the conductivity of the nanowire¹⁹⁰, but still requires further detailed studies. Combined with the redshift of FX emission, the enhanced contribution of FX-1LO leads to a remarkable change of the emission profile. And the ratio of FX-2LO to FX-1LO in curved part was decreased to one fourth of that observed in straight part, which attests the weakening coupling strength of exciton-LO phonon as bending the nanowire. So the comparison between **Figure 6.3a** and **b** provides a new insight in such a relationship: tensile strain, induced by bending the nanowire, is expected to suppress the *local* exciton–LO-phonon coupling.

To confirm this, spatially resolved PL spectra along the axis of a long nanowire were performed using a confocal micro-spectrometer at room temperature. The diameter of the nanowire is 60 nm with 20 μm in length (shown in **Figure 6.4a**), illustrating the extreme flexibility of the nanowires. As shown in **Figure 6.4b**, the spectra collected

from the positions *A* and *H* exhibit similar lineshapes. So we can deduce that the profile of UV emission is not affected much by the anisotropic orientation of the nanowires, even if the strength can be polarization dependent stemming from the dielectric mismatch between nanowires and their local surrounding environment^{109,191-192}. While for the spectra collected from the straight part to the curved part, as general trend, the line width decreases as the peak energy position shifts towards lower energies. The local PL spectra present at least two important points. First, the near-band-edge peak position shows significant bending-induced redshift. Second, the spectrum profile changes accompanied with macroscopic bending of the nanowire. From the fitting results, **Figure 6.5** plots the peak energy of FX corresponding to the different positions along the bent nanowire. Contrast to the normal pressure-induced blueshift¹⁹³⁻¹⁹⁵, an obvious redshift can be observed for the near-band-edge FX emission. In this case, we proposed that a uniaxial tensile strain can be dominated when a bending deformation is applied on the ZnO nanowire, which is in good agreement with our Raman measurement and theoretical prediction from ref. 174. As shown in **Figure 6.5**, the I_{2LO}/I_{LO} decreases with increase in the curvature. More than 20 nanowires were investigated, and all of them show the same behavior. In addition, for most of the samples, the same trend can be observed for I_{LO}/I_{FX} . All these results indicate the reduction of exciton-LO phonon interaction on the bending of ZnO nanowires. In the future, micro-PL measurement at low temperature could be expected. The difference in the strength of exciton-phonon coupling could have significant effects on the optical and transport properties of electrons in

semiconductor.¹⁹⁶⁻¹⁹⁷ We also tried to investigate the effect of bend radius, and nanowire thickness. However, due to the instrument resolution, we could not get a quantitative conclusion.

Figure 6.4 (a) SEM image of an individual bent ZnO nanowire dispersed on SiO₂/Si substrate. (b) PL spectra collected from different positions of the nanowire.

We have also collected the second-order Raman spectra of the LO phonon from different positions of a nanowire. Careful analysis of the resonant Raman spectrum was performed by the peak fitting, as shown in **Figure 6.6**. The inset table summarizes the relevant data for ZnO LO-phonon Raman bands. As we can see, the position of the LO phonon from the bending part is shifted due to the tensile strain effect. Even if there is an obvious photo-induced luminescence baseline (LB), the ratio of LO overtone is significantly reduced from 0.64 to 0.54, which is consistent to the trend observed in micro-PL studies. More conclusive evidence can be expected using resonant Raman mapping and low-temperature microphotoluminescence

measurement.

Figure 6.5 Photon energy of FX, I_{2LO}/I_{1LO} and I_{1LO}/I_{FX} as a function of position along the nanowire.

Figure 6.6 UV Resonant Raman modes from straight (a) and bending (b) parts of an individual nanowire.

It should be pointed out that for optical phonon both deformation potential (microscopic distortions) and the Fröhlich interaction can contribute to the matrix element of exciton-phonon interaction.¹⁹⁷ Through the uniaxial tensile strain (which

will lead to the increase of the lattice constant along the c -axis), the microscopic relative displacement (u/c_0 , where c_0 is the distance between the two atoms inside the primitive unit cell, and u is the relative displacement between atoms along the c -axis associated with $A_1(LO)$ phonon) of the charged atoms within the primitive cell decreases with increasing the bending deformation. So the phonon-exciton interaction can be reduced. Another reason for the decreased coupling is the different confining potentials for the electron and hole wave functions. For an exciton the polar coupling strength is proportional to the squared absolute value of the Fourier transformed difference of the probability densities of electron and hole.¹⁹⁸ With decreasing diameter the influence of surface-related effects becomes increasingly. Wang et al.¹⁷³ reported an electric potential can be produced by the piezoelectric effect and the trapping of electrons at the curved interfaces of the nanowire. This effect might result in the influence of the confining potential on the exciton wave function, especially for the surface region. In this case, it makes the exciton less polar, reducing the coupling strength with the polar lattice via the Fröhlich interaction. On the other hand, taking into account of the bending-induced surface defects, the trapping of exciton at surface located defects results into a reduction of the excited-state lifetime, which can cause a decrease of the exciton-phonon coupling¹⁹⁹. Though the presented model might be considered to be very crude, it can be regarded as a first step for further study of the *local* interplay among mechanical deformation and exciton-phonon coupling in one-dimensional nanostructures.

6.3 Conclusion

In summary, the micro- Raman and photoluminescent properties of individual bent ZnO nanowire were studied. The presence of tensile strain was analyzed by the relative shift of the phonon modes. Using spatially resolved PL experiments, it is found that the ratio of FX-2LO to FX-1LO emission can be suppressed in nanowires due to the bending effect. Recently, the correlation between exciton-phonon coupling and electrical conductivity for ZnO epilayers was investigated²⁰⁰. The possibility to engineer the local phonon-exciton coupling via curving the nanowire provides a unique approach to optimize the electrical and optical properties of a semiconductor nanostructure, which suggests the potential applications of ZnO nanowires as nanoelectromechanical sensors.

Chapter 7 Reversible UV-light-induced Ultra-hydrophobic to Ultra-hydrophilic Transition in α -Fe₂O₃ Nanoflakes Film

As we discussed in chapter 2, micro/nanometer-scale roughness can intensify the surface wettability. So it is proposed that the unique surface characteristic of nanomaterial can imbue the nanostructure with new collective properties. In this chapter, we will cover some research on the understanding of UV responsive α -Fe₂O₃ surface.

7.1 Introduction

With the development of smart devices, great attention has been paid to functional surfaces with tunable wettability.²⁰¹⁻²⁰³ Recently, most studies aim to develop reversible control by applying external-stimuli, including electrical potential²⁰⁴⁻²⁰⁵, photo-illumination²⁰⁶, thermal-energy²⁰⁷ and changes to the surrounding environment²⁰⁸, such as pH value or the presence of organic or inorganic liquids. These techniques promise to stimulate the development of microsystems, materials science, biotechnology and medicine.²⁰⁹ Conventionally, the wetting behavior can be controlled by modifying the surface with organic compounds.²¹⁰ However, due to the poor chemical and thermal stabilities of organic coatings, it is difficult to achieve long-term durability. Additionally, variations in the geometrical structure of a solid surface can influence the contact angle of materials. In this case, however, the

structures may be more susceptible to mechanical damage.²¹¹ Molecular-scale understanding and manipulation of the wetting behavior of water on solids remain a fundamental challenge.

Various transition-metal oxides, such as TiO_2 ,²¹² ZnO ,²¹³ WO_3 ,²¹⁴ and V_2O_5 ,²¹⁵ have been known to exhibit photo-induced hydrophilicity as a result of ultraviolet (UV) irradiation. This type of reversible switching has aroused great interest in both fundamental research as well as practical applications. Hematite ($\alpha\text{-Fe}_2\text{O}_3$), the most stable iron oxide under ambient conditions, is a good candidate for technological applications such as gas sensors²¹⁶, lithium ion battery electrodes⁸² and field emission displays²¹⁷. Zhu²¹⁸ and Lu²¹⁹ employed different methods for the fabrication of Fe_2O_3 nanostructures, which all exhibited excellent wetting. Distinguished from these results, herein, we introduce a facile method to fabricate $\alpha\text{-Fe}_2\text{O}_3$ surfaces with a wettability that can be switched from ultra-hydrophobicity to super-hydrophilicity and vice versa with UV irradiation and dark storage, respectively. Combined with the unique magnetic²²⁰ and electrical²²¹ properties of $\alpha\text{-Fe}_2\text{O}_3$, this type of interesting photo-induced wetting phenomena probably opens a new field in multifunctional microfluidic devices and switches research.

7.2 Experimental Details and Results

A cleaned piece of Fe foil ($10\times10\times0.25\text{mm}$) with a purity of 99.99% (Aldrich) was heated on a hotplate under ambient conditions. The growth temperature was 350°C and the growth duration was fixed as 10 h.⁸¹ After being cooled down to room

temperature naturally, materials produce a superhydrophilic surface. At this instance, the water droplet forms a contact angle of less than 5° within 0.5 s. This observation can be explained by the Wenzel's Equation⁵⁹, as follows

$$\cos \theta_A = r \cos \theta \quad (7-1)$$

where θ and θ_A are the contact angles on a flat and rough surface, respectively. This equation indicates that the surface roughness, r , enhances the hydrophobicity of dewetting surfaces ($\theta > 90^\circ$) and hydrophilicity of wetting surfaces ($\theta < 90^\circ$) since the magnitude of r is always greater than unity. As a polar material with water contact angle of 30° for the smooth surface²²², the α -Fe₂O₃ nanoflake film, possessing a large surface roughness which is confirmed by field-emission scanning electron microscope (**Figure 7.1**), displays the contact angle of water as 0°.

Figure 7.1 FE-SEM image of the as-grown sample.

In addition, we found that the contact angle of the film gradually increases with time. The film became hydrophobic with a contact angle about 130° in 7 days. The origin of the contact angle increase with time is attributed to the adsorption of organic substances from the atmosphere²²³. It is further proved when the film was introduced

into a vacuum chamber, that the water contact angle increment rate was remarkably accelerated and the surface became ultra-hydrophobic with the contact angle of 160°, compared with 0° for the sample stored under Nitrogen atmosphere. Due to the strong chemisorption²²⁴ of Fe²⁺ defect sites in the high-energy surface of α -Fe₂O₃, the organic molecules such as oil droplets from vacuum pumps can be attached on the surface, which will make the sample attain high hydrophobicity. The adsorption species are also confirmed by our X-ray photoelectron spectroscopy (XPS) study, which will be discussed later.

Based on Young-Dupré equation²²⁵, given by

$$W_{sl} = \gamma_{lv}(1 + \cos \theta) \quad (7-2)$$

where W_{sl} and θ refer to the work of adhesion and contact angle between solid and liquid, and we denote the liquid-vapor interfacial energy as γ_{lv} , for a given value of γ_{lv} , the adhesion between the liquid and solid decreases as the contact angle increases. The bouncing of a droplet is achieved on ultrahydrophobic surface. The behaviors of a water droplet falling freely on α -Fe₂O₃ nanostructures surface are shown dynamically in **Figure 7.2**. To the best of our knowledge, this is the first reported observation of dewetting properties of α -Fe₂O₃ nanostructures.

In this work, in addition to the above-mentioned dewetting properties of α -Fe₂O₃ nanoflakes film, we were surprised to find that the wettability can be reversibly switched by alternation of UV (254 nm) irradiation and dark storage. After exposure to UV light (obtained from a 15 W Hg lamp centered at 254 nm) for 3-4 hours, the contact angle was found to be about 0°, which shows that the sample switched from

the hydrophobic to the hydrophilic state. Besides, when the superhydrophilic substrate was kept in the dark for 7 days, its wettability recovered to its pristine hydrophobic state, and the reverse process took place with full reproducibility over four cycles (Figure 7.3).

Figure 7.2 Photoresponsive wettability changes for water droplet profiles.

Figure 7.3 Reversible wettability transitions under the alternation of UV irradiation and dark storage.

In general, the wettability conversion of inorganic materials is attributed to the material being naturally hydrophobic, becoming wetted after the UV-induced generation of free electrons or holes on the material surface which results in the hydroxyl adsorption.²²⁶ Surprisingly, we found that the sample maintains hydrophobicity even when exposed to 365 nm (3.4 eV) light, as shown in **Figure 7.4**, even if the bandgap of hematite is only 2.2 eV.²²⁷ So the role of Fe_2O_3 on amphiphilic character of the sample can be ruled out.

Figure 7.4 Time-dependant change of contact angle after illumination with different wavelengths. The contact angle of water droplets as a function of heat-during time at 90 °C was also shown in order to distinguish the thermal effect from the light-irradiation effect.

7.3 XPS Analysis and Discussions

Figure 7.5 Peak deconvolution analysis of the background-subtracted X-ray photoelectron spectra before and after UV irradiation: (a) the O 1s level; (b) the C 1s peak region. The inset shows the calibrated spectra using the O 1s peak of 530.2 eV.

To explain these phenomena, XPS analysis was carried out on the samples. The Shirley background-subtracted spectra for the sample are found in **Figure 7.5**. No

significant changes in intensity of $\text{OH}^\cdot$ were observed in the binding energy of the O 1s peak after UV exposure (shown in **Figure 7.5a**), since the valence band of Fe_2O_3 is more negative than the redox potential necessary for the generation of $\text{OH}^\cdot$ radicals²²². However, the C 1s bands (inset of **Figure 7.5b**) are gradually attenuated under light (the C 1s peak being calibrated using the O 1s peak), demonstrating the decomposition of adsorbed organics. The C 1s spectroscopy of the original specimens includes three absorption peaks, C-H/C, C-O and C=O, which denotes the existence of organic pollutants. As shown in **Figure 7.5b**, the hydrocarbon band decreased dramatically compared to the band corresponding to the carbonyl. It is known that hydrocarbon tail serves as a hydrophobic region and the carbonyl group as a hydrophilic region. Therefore, the ratio of C-H to C=O will influence the wettability of the sample.

In order to explore the effect of iron ions under UV irradiation, high-resolution XPS of the Fe $2p_{3/2}$ before and after the UV irradiation were investigated (**Figure 7.6**). The spectral shape and its intensity in XPS indicate the character of chemical bonding or the degree of oxidation of the selectively probed atoms.²²⁸ It can be seen that the intensity of the shoulder at the higher binding energy of the peak was significantly increased after the UV exposure. By curve fitting of the spectra, the ionic ratio of $\text{Fe}^{2+}:\text{Fe}^{3+}$ was found to be 0.173 after UV illumination compared to 0.448 before exposure under UV (The intensity ratio is determined using the Fe^{2+} and Fe^{3+} peak areas after subtracting a Shirley background). And it is recoverable when the sample was stored in dark for 7 days. UV irradiation results in decrease of the surface Fe^{2+}

ions. Combined with the CA evolution under 365 nm illumination, we propose a mechanism of the reversible wettability as follows.

Figure 7.6 Peak deconvolution analysis of the background-subtracted XPS for Fe 2p_{3/2}.

Due to the abrupt atom arrangements on the surface, there are many Fe²⁺ defects at the surface. These defects presumably influence the affinity of the surface to organic molecules in their surroundings. In this way, the defect sites were healed by the adsorption species and thereby resulted in the formation of hydrophobic domains. Even if Fe₂O₃ is inert in photocatalysis²²², Fe²⁺ exhibits different surface chemistry compared to Fe³⁺ cations, and offers the potential to catalyze heterogeneous photochemical reactions. The data indicates that after UV illumination (<280nm), Fe²⁺ produces the excited state *Fe²⁺.²²⁹ The excited *Fe²⁺ ions themselves are oxidized back to Fe³⁺ with the decomposition of organic pollutants. This leads to the conclusion that the nanoscale separation between the organic molecules and Fe²⁺

defects accounts for the highly amphiphilic character of the Fe_2O_3 surfaces. During storage in the dark, some Fe^{2+} sites will be present due to thermodynamic considerations. Since the exposure of the surface tends to increase the adsorption of organic molecules, the hydrophobicity of the $\alpha\text{-Fe}_2\text{O}_3$ surface increases, that is, the surface recovers to the superhydrophobic state.

7.4 Summary

In conclusion, a facile method for the fabrication of smart surfaces has been reported. Reversible super-hydrophobicity to super-hydrophilicity transition of $\alpha\text{-Fe}_2\text{O}_3$ was observed and intelligently controlled by alternation of UV illumination and dark storage. XPS spectroscopy provides a way to investigate the conversion of the surface wettability. The combined results show that the transition is mainly due to the adsorption and photocatalytic properties of Fe^{2+} defects. We believe that the discovery of the new phenomena will help to determine and clarify the microscopic mechanism for this macroscopic observation and will pave the way for new applications.

Chapter 8 Summary and Future Work

In this thesis, we focused on the optical characterizations of metal-oxide nanomaterials with the aim to provide fundamental understanding of the micro-physical properties of individual nanostructures. The major accomplishments and contributions to the scientific community reported in this thesis include:

8.1 Summary of the Dissertation

In the first part, high-aspect-ratio V_2O_5 nanoribbons have been synthesized by thermal vapor deposition technique. Our micro-photoluminescence results revealed that the nanoribbons can serve as effective active optical waveguides. In addition, the observation of strong Raman signals collected at the end of ribbon indicate that the unique nanostructure could play vital roles in Raman amplifiers and other nonlinear photonic components. Further, spatially resolved and polarized micro-Raman spectroscopy has been performed on individual V_2O_5 waveguiding nanoribbons. It established that the Raman-antenna patterns are strongly correlated to the *local* positions of the sample, which gives rise to a pronounced intensity contrast in the polarized mapping for certain phonon modes. The suppressed phonon signals in the body of a ribbon can be enhanced at the end facets, resulting from the effective waveguiding propagation along the nanoribbon and strong local electric field intensity at the ends.

In Chapter 5, we described a simple but effective way to control the orientational

arrangement of MoO₃ nanoflakes, which offers an opportunity to investigate the anisotropic properties of different crystallographic faces. According to the polarized micro-Raman spectra, oxygen vacancies preferred to be located at the sharp side edges of the lamella. Ascribing to the unique structural geometry and the oxygen-defects induced reduction of work function, the electron field-emission properties on the samples show that the erected MoO₃ nanoflakes are potential candidates for cold-cathode-based electronics. Strong optical birefringence properties of samples are also observed for the first time.

Then by confocal micro- Raman and photoluminescence spectroscopy, we studied bending effects on optical properties of individual ZnO nanowires. It is shown that local tensile strain can be introduced by bending the nanowire. The strain is expected to reduce the band gap on the bent part and modify the local phonon-exciton interaction, which is determined by the intensity ratio of the second order LO phonon replica of free exciton (FX-2LO) to the first order process (FX-1LO). Our results may provide insight into the modulation of *local* electrical and optical properties by deforming the nanostructures.

Finally, remarkable surface wettability transition of α -Fe₂O₃ nanostructures can be achieved by ultraviolet (UV) illumination in Chapter 7. The distinctive properties of surface defects are disclosed by X-ray photoelectron spectroscopy (XPS) analysis. The nanoscale adsorption and photocatalytic properties of Fe²⁺ defects account for the highly amphiphilic character of the surfaces.

8.2 Future Work

This work can be extended in the following ways:

- 1) Nanomaterial fabrication for applications. Even if several metal-oxide nanomaterials have been fabricated, to synthesize semiconductor nanostructures in large quantities and high qualities is an unavoidable direction. For example, to accurately position nanowires is a requirement for photonic crystal cavities based on nanowire arrays. In this case, the enhanced light-trapping ability provides advantageous optical properties for photovoltaic applications. Besides, further work is in progress to fully explore the optical behaviors of guiding nanoribbons, especially with respect to their potential to exhibit nonlinear properties and sensing.
- 2) Size effect on the individual nanostructures. To obtain additional information on the nanostructure, more experimental analysis and simulation work can be done to quantitatively study the size effects. Size-dependent photoluminescence, waveguiding dispersion and tip effects in V_2O_5 nanoribbon optical cavities, mechanical deformation induced alteration in energy structure and phonon-exciton interaction can be included in the further work, which is critical for the future practical applications.

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