Nonlinear Optical Properties of CdS Semiconductor nanowires

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Abstract. In this work, we report on the nonlinear optical properties in single Cadmium sulfide nanowires (CdS NWs). The high quality growth of CdS semiconductor nanowires were synthesized by chemical vapor deposition (CVD) method. The as-obtained products were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), and the energy dispersive X-ray spectrom (EDS) was used to determine the specific elemental distribution and show purity of the CdS semiconductor nanowires. The excitation of femtosecond laser(800 nm, 50 fs, 80 MHz) was used to study the nonlinear optical properties of CdS nanowires, such as the Second Harmonic Generation (SHG) and optical waveguide effect. CdS NW has a second harmonic generation with a blue emission bands at a wavelength of 400 nm. Finally, based on the dark field image of the CCD taken and combined with the spectrum, it is proved that CdS NW has an optical waveguide effect.

Keywords: Cadmium sulfide (CdS); nanowires (NWs); Chemical Vapor Deposition (CVD); Waveguide; Second-Harmonic Generation (SHG).

1.Introduction.

Knowing the nonlinear optical properties of semiconductor nanomaterials leads to the developing potential applications in nanophotonics devices system and the perfect sciences area[1]. Nonlinear optical Second – harmonic generation has a great role in semiconductor nanomaterials and nanoscience. It is a nonlinear optical process in which two photons of one wavelength are interacted to form a single photon at half the wavelength and at double frequency $2\omega$ [2]. The mechanism of SHG in semiconductor nanowires is a semiconductor nanowire optically excited at the fundamental frequency $\omega$, it emits the optical frequency at the double frequency $2\omega$. This provides a convenient and practical means to obtain blue emission from a near- infrared laser.[3]. Second – Harmonic Generation in semiconductor nanomaterials esspially in semiconductor nanowires structure such as CdS, CdO. ZnS and ZnO nanowires have been specific used for many potential applications such as optical devices system, optical microscopy [4,5] optical photo catalytic, and optoelectronic fields [6,7].
Cadmium sulfide CdS is a kind of very important and practical direct band-gap semiconductor compound in II-VI Group with its bandwidth at room temperature of 2.42eV. [8]. Moreover, CdS has important application prospect due to their optoelectronic performance, such as LEDs, nanolasers and optoelectronic detectors in the visible spectrum range [9]. Due to the unique physical and chemical properties, it is used as the window material of the solar cell. Meanwhile, it has high infrared transmittance and hence has a very extensive research value in light absorption, photoluminescence, nonlinear optics, photovoltaic conversion, photochemical catalysis, stimulated radiation, laser application and other fields because of its excellent optical performance. Featured with low work function, high refractive index and mobility, high chemical and thermal stability, high transmission rate and prominent piezoelectric properties, etc., CdS has a very distinct advantage in the application to flat-panel display, field emitter, nonlinear optical devices, transistor, optical detector, optical waveguides, laser and other devices. [10-13].

In this report, we report the non-linear optical properties of CdS nanowire. The CdS nanowire was synthesized by using chemical precipitation method. X-ray diffraction pattern exhibited that the synthesized product has a high purity and the diffraction peak is very sharp indicating that CdS NW has good crystallinity in addition, the (002) peak particularly pointed sharp, so the preferred growth direction of the material is (002). The SEM image of a single CdS nanowire shows that the nanowire is clean and the diameter is uniform along the wire axis. EDS spectrum shows only target elements which reveal that the sample is in good purity. the EDS analysis was performed in order to show the purity of CdS nanowires .the EDS spectrum of CdS nanowire which exhibits only the characteristic peaks of Cd and S species. No other peaks observed in the spectrum indicate the purity of the samples. An optical confocal microscope configuration was used for optical measurements at room temperature. A femtosecond laser(800 nm, 50 fs, 80 MHz) was used to study the nonlinear optical properties of CdS nanowires, such as the Second Harmonic Generation(SHG) and optical waveguide effect.

2. Experimental Details:
CdS nanowires were synthesized by chemical vapor deposition (CVD) using a simple conventional tube furnace with a 50 mm inner diameter quartz tube, High purity powder (Alfa Aesar ,purity 99.99%) was used as a precursor and was put into a quartz boat that was placed in the center of a tube furnace .Patterned Au thin film coated silicon substrates were placed downstream of the source materials, serving as the deposition substrates. After the tube was sealed, a carrier gas of of pure argon was fled at a flow rate of 50 Scem..Finally, a yellow products was deposited on Si substrate.
Figure 1. Shows the tube furnace of CVD system.

The collected products were characterized by a scanning electron microscopy (SEM, JSM-6701 F), high and low-resolution transmission electron microscopy (HRTEM, Tecnai G220) and X-ray diffraction (XRD, X’Pert PRO, PANalytical B.V., Netherlands), and EDS Figure 2.

Figure 2. (a) low magnification SEM image, (b) high magnification SEM image of CdS nanowires, (c) x-ray diffraction of CdS NWs, and (d) EDS of CdS NWs.

Figure 2 (a) is low magnification SEM image of CdS nanowires, one can find large quantities of wire like structures covered on Si substrate. Figure 2 (b) shows high magnified SEM image of CdS nanowires, this figure shows that the product consists of nanowires with a diameter of Ca.45 nm and a length up to several decades, which represent the high quality of the as-obtained of CdS NWs with uniform diameters and smooth surfaces Figure 2(c) shows X-ray diffraction XRD pattern of CdS NWs. Utilize X’Pert HighScore Plus software. All diffraction peaks can be indexed as hexagonal wurtzite structured CdS with lattice constant of a=0.4141 nm and c= 0.6720 nm be JCPDS card:41-1049 [14]. Suggesting that the synthesized product has a high purity and the diffraction peak is very sharp indicating that CdS NW has good crystallinity in addition, the (002) peak particularly pointed sharp,
so the preferred growth direction of the material is (002). Figure 2(d) shows the energy dispersive X-ray spectrum (EDS) of CdS nanowire which exhibits only the characteristic peaks of Cd and S species. No other peaks observed in the spectrum indicates the purity of the CdS NWs.

3. Optical Waveguide Effect of Cadmium sulfide Nanowires
The one-dimensional semiconductor nanostructure has axial dimension is large and the radial dimension is smaller or nearly equal to the visible wavelength. So, the photon is under the confinement effect along the radial direction and can only transmit along the axial direction. Hence, the one-dimensional semiconductor nanostructure may produce optical waveguide effect and have the functions of optical waveguide devices[15]. The waveguide generated by the semiconductor nanostructure is from spontaneous light, which is conducive to coupling and can greatly reduce the optical loss. Besides, because the semiconductor structure has large refractive index, its refractivity with the air can help enhance the binding effect of the light beam[16,17]. A titanium sapphire femtosecond laser at 800nm wavelength was radiated a single CdS NWs to obtain fluorescence spectra. Figure 3. In the figure we can see that there is a very strong luminescence peak at the nanowire 537.8 nm, which is half-high The width is relatively small, the emission peak originates from the intrinsic emission of the spontaneous emission of sulfide free excitons at room temperature, and the peak spectral curve It is very smooth and no other impurity peaks appear, indicating that the grown nanowires have no defects or impurities. Luminous spectrum The sample quality is represent to a pure single crystal and has no defects As shown in the inset of Fig. 3, the bright field and dark field images taken by the CCD under the optical confocal microscopy system. For example, it can be observed from the bright field image that the nanowire is very smooth and flat at both ends, which is conducive to forming a resonant cavity. When the laser is focused in a certain position in the nanowire, it can be seen from the dark field image that the cadmuim sulfide has a strong two-photon excitation. The green light is emitted and propagates along the vertical axis and emits a significant spot at both ends of the nanowire, while in other parts of the nanowire. The light is very weak and almost impossible to observe, indicating that the sulfur, and cadmium nanomaterials have very good optical waveguide properties. Become a good optical waveguide device

![Figure 3. Optical Waveguide Spectrum of Cadmium sulfide Nanowires](image)

Figure 3. Optical Waveguide Spectrum of Cadmium sulfide Nanowires
4. Second-Harmonic Generation Experiment

An optical confocal microscope configuration was used for SHG experiment at room temperature. A femtosecond laser (800 nm, 50 fs, 80 MHz) was used to study the nonlinear optical SHG of CdS nanowires. Figure 4a schematic diagram of the Second –Harmonic Generation experiment setup. A mode-locked Ti sapphire femtosecond laser system (Tsunami, Spectra-Physics, ~800 nm, 50 fs and 80 MHz) was used as the pumping source. The intensity of the pumping laser beam was adjusted by combining a half-wave plate (A1) and a polarization beam splitter (B). The pumping laser polarization direction was controlled by another half-wave plate (A2). A microscope objective (Olympus, 0.65 NA, 40×) focused the pumping laser onto the sample with a focal spot diameter of ~4 μm. The transmitted SHG signal originated from CdS NWs was collected by another identical objective and subsequently imported to a CCD or spectrometer (Princeton Instruments Acton 2500i with Pixis CCD camera). A 750-nm short-pass filter (C) filtered out the pumping laser. The polarization-dependent SHG response of the single CdS NWs was measured by rotating the polarization direction of the pumping laser with A2. The spectrum in Fig.4b presents a strong peak at 400nm, which is exactly half wavelength of the pumping laser. Inset in (b) is the bright-field and dark-field images taken with a CCD camera. where the power density of the exciting light is 512.5kW/cm².

![Figure 4](image_url)

**Figure 4.** (a) Schematic diagram of the Second –Harmonic Generation experiment setup of CdS NW. A1 and A2 are half-wave plates, B is a polarizer, and 750 nm short pass filter, M1 is the transparent visible light mirror at 800 nm, the objective lens (40×, numerical aperture 0.65) was used to focus the pumping laser, and the transmitted SHG signal was collected by another 40x objective. The signal spectrum in Figure 4(b), presents a strong peak at 400nm, which is exactly the frequency doubling signal of the pumping laser. Inset in (b) is the bright-field and dark-field images taken with a CCD camera, where the power density of the exciting light is 512.5kW/cm².

5. Conclusions:

In conclusion, the femtosecond lasers have played a very important role in the promotion of semiconducting nanomaterials. The nonlinear optical properties of the nanowires were investigated using an optical confocal microscope platform. CdS nanowires have been synthesized by chemical vapor deposition (CVD). The structural characterization of the samples observed by SEM, XRD, and EDS. A femtosecond laser (800 nm, 50 fs, 80 MHz) was used to study the nonlinear optical properties.
of CdS nanowires, such as the Second Harmonic Generation (SHG) and optical waveguide effect. CdS NW has a second harmonic generation with a blue emission bands at a wavelength of 400 nm. Finally, based on the dark field image of the CCD taken and combined with the spectrum, it is proved that CdS NW has an optical waveguide effect.

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