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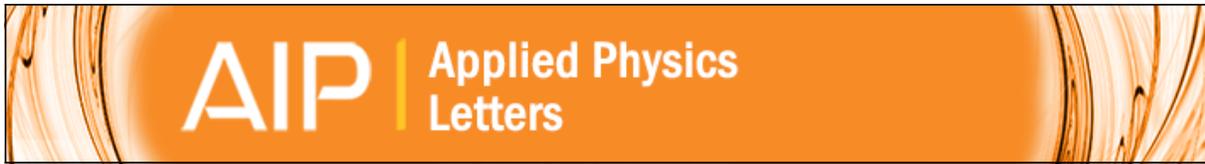
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We develop a technique to measure the absorption spectrum of individual nanowires with the supercontinuum laser based Fourier transform spectroscopy. It employs photocurrent of a nanowire as the signal for Fourier transform spectroscopy. We demonstrate this technique in obtaining absorption spectrum of individual cadmium selenide nanowires, and determine the nanowires absorption bandgap of 1.75 eV. This technique has high detection sensitivity. Potentially it will be able to measure absorption cross-section as small as 19 nm^2 per μm for a focus laser spot of 1 μm, and could be a general method to detect the absorption spectrum of individual quasi-one-dimensional nanomaterials. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4739786]

The quasi-one-dimensional (1D) nanostructures, including carbon nanotubes, graphene nanoribbons, and semiconductor nanowires, have attracted intensive attentions in applications of electronics, optoelectronics, and photonics.[1–4] In contrast to their bulk counterparts, the fundamental physical properties of these nanomaterials are extremely sensitive to their specific structures and surface states. Therefore, the characterization at the single nano-object level is highly desirable to understand structure-specific properties of nanomaterials. Optical absorption, as one of the most significant optical properties, provides fundamental information on the electronics structure of materials and evaluating the quantum efficiency for other absorption related processes.[5–8] However, measurements of optical absorption on individual nano-object are often challenging by conventional means mainly due to their small absorption signal level.[9,10] Cadmium selenide (CdSe) nanowire is a prototype of quasi-1D semiconductor nanomaterials with a bandgap in the visible range and a promising candidate for next generation solar cell materials.[11–13] However, most absorption studies on CdSe nanowires are performed on ensemble samples[14–16] and reliable absorption measurement at single-nanowire level is still missing.

In this letter, we demonstrate a method to measure the absorption spectrum of individual CdSe nanowires using a supercontinuum laser light source based Fourier transform (FT) photocurrent spectrometer. FT photocurrent spectroscopy as a sensitive method has been used to determine the spectral resolved absorption coefficient of thin film solar cell.[17] Recently, this technique is also demonstrated as a powerful tool in high resolution photocurrent mapping[18] as well as the characterization of self assembled quantum-dot[19] and nanowire ensemble based devices.[20] Combining with the supercontinuum laser source, the FT photocurrent spectroscopy exhibits several unique advantages in our single nanowire absorption measurement. (1) The supercontinuum light source is commercially available nowadays. It has broad spectral range (450–1600 nm) like a light bulb, and has high brightness as a laser. It can be readily focused down to the diffraction limited size, which is prerequisite to study individual nanomaterials. (2) FT spectroscopy employs the photocurrent of individual CdSe nanowires as the signal in this study. Since the photocurrent is directly proportional to the number of absorbed photons,[8,13,17] this FT technique is background free. It is a great advantage over the conventional approach in measuring the small transmission change in a large transmission background, where the background fluctuations usually bury the small signal. In addition, FT spectroscopy is highly compatible with broadband illumination with its intrinsic high throughput advantage, and it has high spectral resolution (better than 0.1 nm in visible range).[21] Using this technique, we obtained absorption spectra of individual CdSe nanowires. It shows a nanowire absorption bandgap of 1.75 eV. This bandgap value is in agreement with independent photoluminescence measurement on the same nanowire. Further analysis on the detection limit shows that our method can be applied to measure the absorption spectrum of general individual quasi-1D nanomaterials.

Figure 1 presents the supercontinuum light source based FT spectrometer setup for measuring absorption spectra of semiconductor nanowires. Similar as conventional FT spectrometers, the key component of our setup is a Michelson interferometer consisting of a beam splitter (BS), a fixed mirror (M$_1$), and a movable mirror (M$_2$). The linear stage carrying the movable mirror has position resolution of 25 nm and travel range of 20 cm that enable our setup perform in the visible range with relative high spectral resolution.[21] The source light emitted from the supercontinuum laser entries into the interferometer and interferes at the output. The interfered light is directed by a mirror (M$_3$) and focused onto the sample (S) through a 20 × objective (O), which can enhance the signal level and permits the illumination only on the nanowire. The focused light is absorbed by nanowire sample that generates a photocurrent signal accordingly. As the movable mirror scans, we obtain a frequency encoded photocurrent signal as a function of position. To record the position of movable mirror, we simultaneously introduce a He-Ne laser into interferometer. The interfering He-Ne laser is reflected by a mirror (M$_4$) and focused by a Len (L). It is

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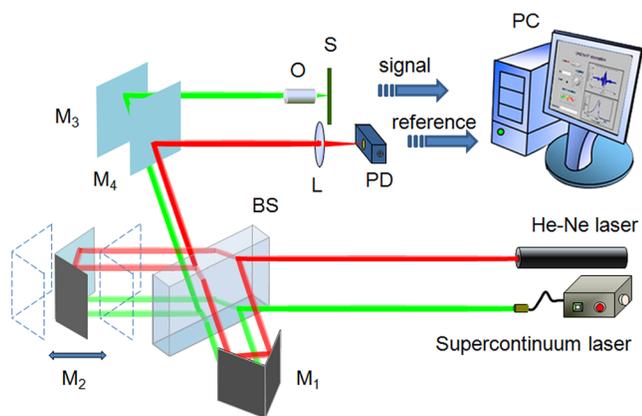
FIG. 1. Experimental scheme of supercontinuum laser based Fourier transform spectrometer for absorption measurement of quasi-one-dimensional individual nanomaterial. BS, beam splitter; M, mirror; O, objective; S, sample; L, lens; PD, silicon photodiode.

finally collected by a silicon photodiode (PD) to extract the stage position. The spectrum of absorbed light is obtained by processing the position dependent photocurrent signal with Fourier transform algorithm by a computer. Similarly, replacing the sample with a silicon photodetector with well-defined absorption response, we can deduce the spectrum of the light source. Absorption spectra of the sample can then be derived by normalizing the Fourier transform of photocurrent signal against the spectrum of the light source.

In the following, we demonstrate this technique to measure absorption spectra of individual CdSe nanowires. The nanowires were grown by chemical vapor deposition (CVD) method following Ref. 22. Briefly, we use CdSe powder (99.999%) as feedstock and gold nanoparticle as catalyst for CVD growth at 700 °C. The as-grown nanowires have diameter in the range of 200 nm to 2 μm with average value of 800 nm. To guide the photocurrent flow of the nanowire, we use standard electron beam lithography followed by metal evaporation to fabricate two electrodes (Au/Cr of 80/10 nm) on individual CdSe nanowires. In the inset of Fig. 2(a), we show an optical microscopic image of our device. The horizontal black line is the nanowire and the left and right ends are metal electrodes.

Due to the depolarization effect arising from structure anisotropy, optical absorption in the nanowire can be significantly modified by geometric effect for light polarization perpendicular to the nanowire. However, absorption for light polarization along the nanowire will not be affected in the

quasi-1D structure with large aspect ratio.[23] Therefore, we have set the light polarization parallel to the nanowire axis in our measurement. We first characterize photocurrent behavior of the CdSe nanowire device. The photocurrent *vs* voltage (I–V) curve of nanowire is shown in Fig. 2(a), where the nanowire is illuminated by a supercontinuum laser with intensity varying from 0 to 1.7 mW/μm². It can be seen that the nanowire device is highly insulating at dark state and the photocurrent increases monotonically with laser power.

For FT spectroscopy, the sampling speed should be slower than the photocurrent response to avoid the signal overlapping. Figure 2(b) shows the time-dependence of the nanowire photocurrent signal with laser illumination. Here, the bias voltage is fixed at 2 V, and the light with intensity of 1.7 mW/μm² is modulated by a square wave at a frequency of 200 Hz. The rise and decay tails obey the logarithmic behavior of $I = I_0[1 - \exp(-t/\tau_{ris})]$ and $I = I_0\exp(-t/\tau_{dec})$, with a rise and decay time constant of $\tau_{ris} = 34\,\mu s$ and $\tau_{dec} = 230\,\mu s$, respectively. We thereby choose 300 μs sampling period in the following FT spectrum measurement. In fact, for nanowire with even longer response time, the FT setup can also work well in the step-scan mode to avoid the detection distortion.

The direct Fourier transform of the frequency encoded CdSe nanowire photocurrent is displayed as the solid curve in Fig. 3(a). The spectrum of the supercontinuum light source is shown as the dashed curve in Fig. 3(a), which is calibrated by using a Si photodiode with known absorption response in place of the CdSe nanowire. The ratio between the CdSe photocurrent response and supercontinuum spectrum yields the absorption spectrum of the nanowire, which is illustrated as the solid curve in Fig. 3(b). The absorption spectrum shows a clear cutoff at around 710 nm, it corresponds to an absorption bandgap of 1.75 eV. This bandgap values can be further verified by obtaining independent photoluminescence spectrum of the same nanowire (dashed curve in Fig. 3(b)). The luminescence spectrum shows a clear peak centered at the same bandgap energy of 1.75 eV (i.e., wavelength of 710 nm). The drop of absorption at shorter wavelength region is attributed to the decreased efficiency of electron-hole pair separation for high energy photon, which is also observed in other nanowire devices.[24,25] The slightly higher fluctuation at shorter wavelength has its origin from the instability of the interferometer, which deteriorates the signal more at shorter wavelengths.[21] The travelling distance of our movable mirror is 2.5 mm, which leads
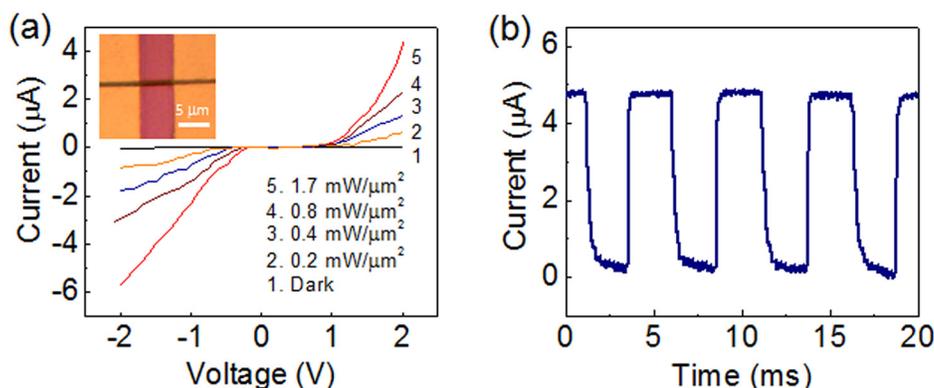

FIG. 2. (a) I–V Curves of CdSe nanowire under light illumination with varying intensities. The inset shows the optical microscopic image of single CdSe nanowire electrical device. (b) Photoresponse time of the nanowire device under a 200 Hz square modulated light illumination. The light intensity is 1.7 mW/μm², and the bias voltage is 2 V. It shows a photocurrent response time less than 300 μs.
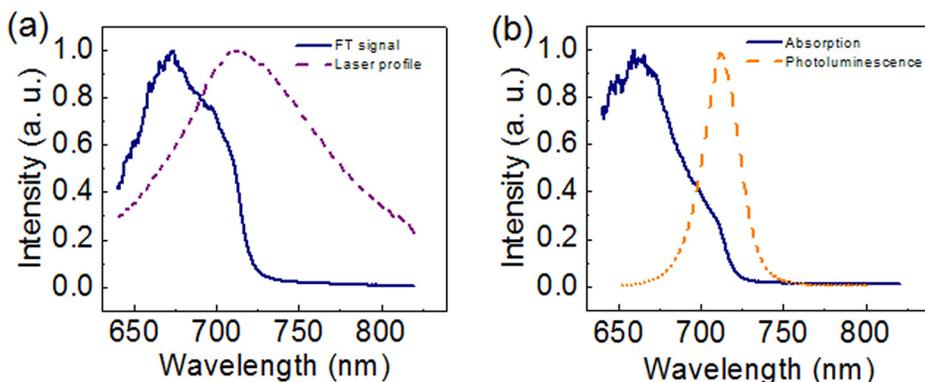
FIG. 3. (a) Direct FT spectrum of frequency encoded CdSe nanowire photocurrent (solid line) and the supercontinuum laser spectrum (dashed line); (b) Normalized FT spectrum by the laser spectrum, i.e., absorption spectrum spectrum of CdSe nanowire (solid line). The dashed line shows photoluminescence spectrum of the same CdSe nanowire. The bandgap was determined to be 1.75 eV by the cutoff wavelength in the absorption spectrum, which is consistent with the peak wavelength of photoluminescence.

to a spectral resolution better than 0.1 nm. This spectral resolution can be further improved by increasing the movable mirror travelling distance if required.[21]

Our technique should be generally applicable to different quasi-1D materials, although we demonstrated here a study of individual CdSe nanowires. Next, we provide a theoretical estimation on the sensitivity of our approach. Assuming an excitation laser focused down to 1 μm, the smallest absorption cross-section of a nano-object that we can measure is determined by[26]

$$\sigma = \sqrt{\pi} \frac{I_{ph}}{e} \frac{h\nu}{\eta P} .\qquad(1)$$

Here, I_{ph} is the smallest photocurrent that we can measure, which is limited by the current noise in the system, e is the electron charge, $h\nu$ is the incident photon energy, η is the quantum efficiency of photon-carrier conversion, and P is the laser power. In our measurement, the laser power is about 1.3 mW and the current noise is 900 pA. Using a typical quantum efficiency of $\eta = 10\%$,[27,28] the detection limit of the absorption cross-section in our setup is around 19 nm^2 per μm length for a 1 μm-size laser spot in 1 s average. Such sensitivity is already high enough to measure most of the quasi-1D nanomaterials, such as single-wall carbon nanotube which has typical absorption cross-section of 110 nm^2 per μm length.[29]

In conclusion, we developed a method to detect the absorption spectrum of individual quasi-1D nanomaterials with supercontinuum laser based Fourier transform spectroscopy. We demonstrated our method by measuring the absorption spectrum of single CdSe nanowires. A bandgap energy of 1.75 eV was found and further confirmed by independent photoluminescence measurement. Our method has high absorption cross-section detection sensitivity and can be used to detect small absorption signals of other individual quasi-1D nanomaterials.

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