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Generation of exciton-polaritons in ZnO microcrystallines using second-harmonic generation

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\textbf{Abstract.} We report an observation and detail mapping of exciton-polaritons (polaritons hereafter) on both lower-polariton and upper-polariton branches in ZnO microcrystallines using second-harmonic generation. Our investigations reveal that those polaritons can be well described by the dispersion curves of nanowires at certain diameter. The polaritons in the tree-like microcrystallines evolve as a function of incident wavelength in a similar fashion as that in a single nanowire. Hence, the origin of polaritons generated in the wire-based microcrystallines is the coupling between the excitons and the nanowire-cavities. The resonance profile of the polaritons reveals that the enhancement is due to the strong coupling between second-harmonic photons and the A, B and C excitons in ZnO. The high photon–polariton conversion efficiency suggests a new strategy for harvesting solar energy.

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1. Introduction

Semiconductor nanowires and microcrystalline form a novel class of natural optical cavities, without employing external mirrors or distributed Bragg reflectors, and thus are promising building blocks for optical and opto-electronic devices\(^1\)–\(^5\), owing to their compact structures, minimized sizes and extraordinary optical properties. Particularly, the wave guiding\(^1\),\(^6\) of ultraviolet (UV) and visible lights with a vacuum wavelength larger than the nanowire diameter and the polariton nanolasing\(^7\)–\(^9\) with an ultralow threshold are two examples of such exciting photonic applications. Polaritons are quasi-particles generated by the strong coupling between excitons in a semiconductor material and photons in a microcavity, which play an important role in understanding light–matter interactions\(^10\)–\(^13\). Unlike two-dimensional (2D) planar microcavities that have been extensively investigated\(^10\)–\(^13\), spatially organized 1D nanowires and their 3D complex structures have been studied far less. To date, the microscopic mechanisms of related optical phenomena in 1D nanowires, e.g. photoluminescence (PL), light–matter interaction (polaritons), polariton lasing and guiding etc have not been clearly delineated.

ZnO nanomaterials\(^14\) provide a unique opportunity to explore the above-mentioned underlying mechanisms for polariton-related phenomena, due to the extremely large oscillator strength (i.e. Rabi splitting\(^15\),\(^16\) of >100 meV from a strong light–matter coupling), stable excitons at room temperature (RT)\(^17\) (i.e. the binding energy of 60 meV comparing with the thermal energy of 26 meV) and a large second-order susceptibility\(^18\) for second-harmonic generation (SHG). It has been previously reported that photons and polaritons in the ZnO nanowires can form whispering-gallery modes (WGMs)\(^19\),\(^20\) at the hexagonal cross-sections, which can greatly increase the light–matter interaction. Furthermore, the use of SHG can provide an efficient way for near-resonant excitation to form the polaritons and, at the same time, reduce the background from the fundamental excitation light. As a wide band-gap semiconductor, ZnO has the wurtzite crystal structure, and the schematic diagram of the excitonic band gaps for the A (3.309 eV), B (3.315 eV) and C (3.355 eV) excitons (at RT) is displayed in figure 1(b). When light beam is normally incident onto a nanowire (\(\mathbf{k} \parallel \mathbf{c}\)) and polarized along the wire (\(\mathbf{E} \parallel \mathbf{c}\)), the electric dipole transitions are such that the C exciton is strongly active, whereas the B exciton is very weak and A exciton is forbidden\(^17\),\(^21\). If the polarization of the incident light is perpendicular to the wire’s \(\mathbf{c}\)-axis (\(\mathbf{E} \perp \mathbf{c}\)), both \(\mathbf{A}\) and \(\mathbf{B}\) excitons are active and the \(\mathbf{C}\) exciton is then forbidden\(^17\).
Figure 1. (a) SEM image of a tree-like ZnO microcrystalline, showing branches of nanowires with lateral size in the range of 50–400 nm and length of about 2–3 µm. (b) Schematic diagram showing excitonic band structure of ZnO, consisting of A, B and C excitons. (c) PL spectrum displaying excitons bounded to deep impurity (2.92 eV), to shallow impurity (3.05 eV), and features of lower polariton (LP, 3.15 eV) and upper polariton (UP, 3.65 eV), when excited by a laser line at 3.44 eV.

2. ZnO nanowires and microcrystallines

The nanowires and wire-based tree-like ZnO microcrystallines used in the investigations were grown on quartz plates through a hydrothermal method [22]. A scanning electron microscopy (SEM) image of such a tree-like structure is shown in figure 1(a). It consists of hexagonally organized six columns of branched nano/microwires, with the lateral sizes of the wires in the range of 50–400 nm and length of about 2–3 µm. Comparing to a conventional 2D microcavity [8–13], the tree-like microcrystalline can be approximated as a quasi-1D system, i.e. each nanowire can be characterized by the wavevector \( k_z \) along the wire’s optical c-axis, which can be aligned in any directions on a 2D plane, but having a sixfold symmetry due to the formed wire branches, whereas \( k_x \) and \( k_y \) in each wire are confined by the lateral size (or...
diameter). Therefore, the dispersion curves in such a tree-like microcrystalline may be described by a 1D nanowire with a variable $k_z$-direction. However, the polarization of the incident light with respect to the wires’ $c$-axes can be in $\mathbf{E} \perp \mathbf{c}$ and $\mathbf{E} \parallel \mathbf{c}$ simultaneously, so one would expect that all three (A, B and C) excitons in ZnO will be involved in the electric dipole transitions when interacting with photons.

While the spatially resolved PL spectroscopy in ZnO-tapered wires shows that the observed WGM polaritons can be described by the dispersion curves from wire sides [18], other studies have claimed that lights can also be emitted predominantly at both ends of the ZnO wires [23, 24]. The spectral shape of polaritons from wire ends reflects polariton eigenmodes consisting of a series of peaks and the spacing between the peaks scales with the inverse of wire length. More recently, polaritons from 1D Fabry–Perot modes (FPMs) and 2D WGMs have been reported [25, 26] to occur separately or simultaneously within the cross-sections of the ZnO wires. All these investigations suggest that the observed polaritons in the micro/nanowires are strongly dependent on the sample growth condition, shapes of the wires and their cross-sections. It has been shown [25, 26] that FPMs can preferentially be observed in thick wires with an elongated wire cross-section lacking hexagonal symmetry, whereas the formation of WGMs requires hexagonal symmetry that can be observed more easily in wires with smaller diameters [25]. In this work, by applying SHG in ZnO nanowires and wire-based microcrystallines, we observed upper-polaritons (UPs) and lower-polaritons (LPs), which can be characterized by dispersion curves for wires with certain diameters (or specific lateral sizes) with the polaritons confined in waveguide-like microcavities. The similarity between the observed polaritons from an individual nanowire and the wire-based microcrystallines, as well as the agreement between the direct mapping of the measured polaritons and the calculated dispersion curves, support the nature and origin of the polaritons in the complex tree-like structure. The observed polaritons reported in this work thus represent an intermediate mixing case between polaritons from WGMs at certain wire diameters and polaritons formed between wire ends (FPMs). The wavevector component along the wire’s optical $c$-axis allows the polaritons to propagate after they are generated at certain diameter and the polaritons can also form WGMs at suitable diameters during propagation.

3. Results and discussion

For comparison between the direct near-resonant excitation and second-harmonic (SH) photon excitation, figure 1(c) displays PL spectrum when the microcrystalline is illuminated by a short-pulse laser at wavelength 360 nm (3.44 eV). The energy difference between excitons B and A, and excitons C and B are 6 and 40 meV, respectively. However, the energy differences between the three peaks below the excitation energy in figure 1(C) are 130 and 100 meV, respectively, which are much bigger than the corresponding energy differences for the three excitons. Therefore, the three peaks should not correspond to the three excitons, or the excitons bounded to the same impurity. The broad peak at 2.92 eV (424 nm) may be attributed to excitons bounded to deep impurities, and the peaks at 3.15 eV (394 nm) and 3.05 eV (406 nm) could be related to the LP (by comparing to the spectra using SH photon excitation) and bounded-excitons, respectively. Since the peak at 3.65 eV (340 nm) is larger in energy than the excitation energy and that of exciton C, it can only be related to the generation of UPs. The spectral positions of the LPs and UPs at 394 and 340 nm, respectively, in figure 1(b) are reasonably close to the spectral positions measured by using SHG in figure 3(a), where the features are
dominated by polaritons with much stronger intensities. The spectral shapes and peak positions in figure 1(c) differ from those in [19, 23, 24], most likely due to different growth conditions, wire sizes, structures and impurities.

In order to avoid the unwanted features related to impurities and explore stronger polariton signals, especially near resonance, excitation with SHG was employed in our investigations. The generated SH photons from ZnO directly couple to the excitons of ZnO, rather than with excitons bounded to the impurities, which results in cleaner and stronger spectral peaks for the generated polaritons. By using SH photons to generate the excitons, we can easily eliminate the background of the strong fundamental pumping field and easily observe the weak features in the spectra due to resonant excitation. Another important benefit from using SHG is the preservation of wavevector from the incident photons to SH photons, i.e. double the wavevector due to the satisfied phase-matching condition. The generated SH photons are confined in the cavities formed in the wires, and the intersection of their dispersion curve with that of the excitons is the resonant energy for the generated polaritons, as shown in figure 2(a). Moreover, the conservation of wavevector from the photon component of the polaritons to the emitted photons makes it feasible to directly map the dispersion curves. Hence, there is a one-to-one correspondence between the SH photon, the formed polariton, and finally, the emitted photon due to the leakage of the polariton, which allows us to access the density of polaritons in the nanowires. In this scenario, instead of adjusting the angle difference between the incident and emitted photons as used in conventional polariton mapping [11–13], we map the dispersion curves by varying wavelength of the incident photons with fixed incident and emission directions, as shown in figure 2(b). Single high-quality nanowire and tree-like microcrystalline structure on quartz substrates were selected and illuminated, respectively, with a laser spot about 40 µm in diameter from a femto-second Ti:sapphire laser (with a spectral width of 15 nm). The emitted photons (from either SHG or polaritons) can be detected either by a photo-multiply tube after passing through a spectrometer or by forming an image on a CCD camera, both with the fundamental incident light filtered.

Away from the exciton–photon strong coupling region, i.e. when the incident SH photon energy is far below the exciton energies, SH photons dominate in the emitted spectra, as shown in figure 2(c). The results are taken from a single ZnO nanowire with $E \parallel c$. The broad spectral peak has a spectral width of about 15 nm full-width at half-maximum (FWHM), reflecting the spectral width of the incident pulse laser. The central wavelength of the observed broad spectrum locates at half of the incident wavelength as a result of SHG, and changes accordingly when the incident wavelength is tuned. In the strong coupling region, i.e. when the energy of the SH photons approaches to that of the excitons, features of SH photons will disappear and the polariton features start to show up and begin to dominate, as shown in figure 2(d). The spectral evolution as a function of the incident wavelength clearly displays a dependence of the polariton energy on the incident wavelength. However, the LP feature from the single nanowire is relatively weak and no UP-related features can be observed.

On the other hand, both LPs and UPs can be clearly observed in the complex tree-like ZnO microcrystallines, which are essential to establish the polariton dispersion curves. The spectral evolutions of the LPs and UPs, as a function of the incident photon wavelength, are shown in figure 3(a). In general, the polariton dispersion curve in ZnO can be described by [17, 19]

$$
\varepsilon(\omega, \mathbf{k}) = \varepsilon_\infty \left(1 + \sum_{j=A,B,C} \Omega_j \frac{\omega_{j,L}^2 - \omega_{j,T}^2}{\omega_{j,T}^2 - \omega(\mathbf{k})^2 - i\omega(\mathbf{k})\gamma_j} \right) = \frac{c^2 k^2}{\omega(\mathbf{k})^2},
$$

(1)
Figure 2. (a) Exciton–polariton dispersion curves of a ZnO nanowire, showing the LP branch (LPB) and the UP branch (UPB). When the confined photons are close in resonance with the excitons, the strong light–matter interaction leads to the formation of exciton–polaritons. (b) The experimental setup. The incident pulse from a mode-locked Ti : sapphire laser can be tuned in the range of 710–890 nm. The emitted photons can form image on a CCD camera and can be recorded by a spectrometer simultaneously. The filters are chosen to shield the fundamental lights from the laser. (c) Features of the SH photons as a function of incident photon wavelength. (d) The spectra displaying evolutions of polaritons at low excitation power, when the energy of the SH photons moves across and in resonant with the ZnO excitons. The spectra are taken for single ZnO nanowire at RT.

where $\varepsilon_{\infty}$ is the background dielectric constant; $\omega_{j,T}$ and $\omega_{j,L}$ are the transverse and longitudinal resonant frequencies, respectively; $\gamma_j$ is the damping constant; $c$ is the speed of light in vacuum; $\Omega_j$ is a prefactor and $j$ stands for A, B or C exciton [17, 19]. ZnO wire of diameter $d$ and length $L$ is reminiscent to a laterally confined microcavity in which the confinement is caused by the refractive index contrast with the surrounding air [16, 27]. In such a cavity, one can further approximate the structure by considering a rectangular cavity with $d \approx d_x \approx d_y \approx d_z$ (SH photon wavelength) and $L \gg \lambda$. In such a case, only one optical mode can be allowed in the confined $x$- and $y$-directions [27]; however, the much longer length along the $z$-direction (the crystal
Figure 3. Direct mapping of the exciton polaritons from measured spectra for a tree-like ZnO microcrystalline at RT. (a) The spectra display evolutions of the LPB and the UPB, as a function of the incident photon wavelength at low excitation power, when the band excitons are on resonance with the confined photons. SHG denotes features in the SH generation. (b) The direct mapping of the dispersion relations for the exciton-polaritons, showing a good agreement with the numerical calculation using a simple nanowire model, with an effective lateral size of 230 nm. Inset is the enlarged region of the dispersion curves at the ‘bottleneck’ region.

The $\hat{c}$-axis) allows $k_z$ to be adjusted as $2\pi/\lambda$. Thus,

$$k = \sqrt{k_x^2 + k_y^2 + k_z^2} = \sqrt{\left(\frac{m_x\pi}{d_x}\right)^2 + \left(\frac{m_y\pi}{d_y}\right)^2 + k_z^2},$$

(2)

where $m_x$ ($m_y$) is the mode number along the $x$-($y$-)direction. In our calculation, the mode number is set to two for simplicity, and $d(=d_x=d_y)$ is used as a fitting parameter. Due to the broad spectral width of the incident light (FWHM of 15 nm), the spectra of the polaritons have the similar width and thus only the peak positions are considered. The model assumes that the total intensity from a microcrystalline structure is a linear summation of contributions from individual wires and any possible interactions among them are neglected. This assumption is justified by looking at the similarity between the spectra displayed in figure 2(d) for a single nanowire and those in figure 3(a) for a complex microcrystalline, and also by considering the reasonable agreement between the direct mapping of polaritons and the dispersion curves as
Figure 4. Comparison of resonance profiles between a microcrystalline and a nanowire. The integrated intensities of polaritons as a function of the incident wavelength, i.e. the resonance profiles, reveal the resonant enhancements at the A, B and C exciton energies. The comparison between the microcrystallines and nanowire shows different photon–polariton conversion efficiencies.

shown in figure 3(b). The lateral size, as a fitting parameter, is determined to be 228 nm. The Rabi splitting between the LP and UP branches in figure 3(b) is about 310 meV, which is more than three times of the value reported in [16] and 1.5 times of the value reported in the most recent result of [25]. It is not surprising that the observed polaritons are located in the so-called energy relaxation ‘bottleneck’ region [11] on the dispersion curves (figure 3(b)). Typically, from the bottleneck region to $k_z = 0$, the energy density of states (DOS) decreases abruptly by four orders of magnitude, whereas the lifetime reduces by two orders of magnitude. Due to the higher DOS and longer lifetime, the polaritons in the bottleneck region are thus easier to accumulate and to be measured.

As shown in equation (1), the strong coupling, and thus the resonant enhancement, occurs when the SH photon energy approaches to the exciton energy. Since $c$-axes of the compositing wires in the tree-like microcrystalline align in different directions on the substrate plane, all the A, B and C excitons should involve in the interactions with the SH photons. As displayed in figure 4, spectral profile from a wire-based microcrystalline reveals the resonant enhancement at the A, B and C excitonic energies. The resonant peaks of the SH photon energy at A, B and C excitons directly reveal the underlying strong coupling between excitons and the cavity-confined SH photons, which strongly support our attribution of the formed polaritons. For a single nanowire with $E \parallel c$, the strong coupling to the C exciton dominates, as shown in figures 2(d) and 4 (lower curve), and the coupling to the B exciton is weak, but still observable, while coupling to the A exciton is absent. The above results are consistent with the predicted selection rules. The normalized integrated intensities in figure 4 are closely related to the crystalline structure, size and quality. Another point worth mentioning is that the integrated intensities of the created polaritons are comparable to those of the SH photons, as shown in figures 2(c), (d) and 3(a). Therefore, polaritons have a high photo-conversion efficiency and high mobility within the crystalline structure, which can further be explored for solar
energy harvesting application. Compared to other semiconductors, ZnO has a uniquely large second-order nonlinear susceptibility, which leads to highly efficient SHG. As a result, the corresponding SH absorption spectrum of ZnO covers a broad spectral range of the sunlight, from UV to infrared. Moreover, ZnO nanomaterials show the second-highest efficiency as solar-cell material after TiO$_2$ \[28\].

4. Conclusion

We have observed LPs in ZnO single nanowire, and both LPs and UPs in wire-based tree-like microcrystallines at RT. The generated exciton polaritons can be characterized by microcavities in 1D ZnO wires with the dispersion curves specified at certain diameter where the confined SH photons are in or near resonance with the excitons. The resonant profiles reveal the nature of the strong coupling between the confined SH photons and the A, B and C excitons in ZnO micro/nanostructures. The broad spectral coverage in generating SH photons and the high photo-polariton efficiency for ZnO materials, together with the high mobility and the ability of propagation over a long distance \[29\] in wires, may be employed to convert and store these photo-converted polaritons electronically with such complex ZnO microstructure as an integrated storage device.

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