

Piezotronic effects on the optical properties of ZnO nanowires

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1. A bent ZnO NW with a diameter of about 310 nm

The PL spectra of a bent ZnO NW with a diameter of about 310 nm are shown in Figure S1. We can also observe significant redshifts for FX_A and D^0X_A in bent regions. And the redshifts increase with increasing strain. However, the shifts of the exciton-phonon replicas $\text{FX}_A - 1\text{LO}$ and $\text{FX}_A - 2\text{LO}$ are not very apparent.

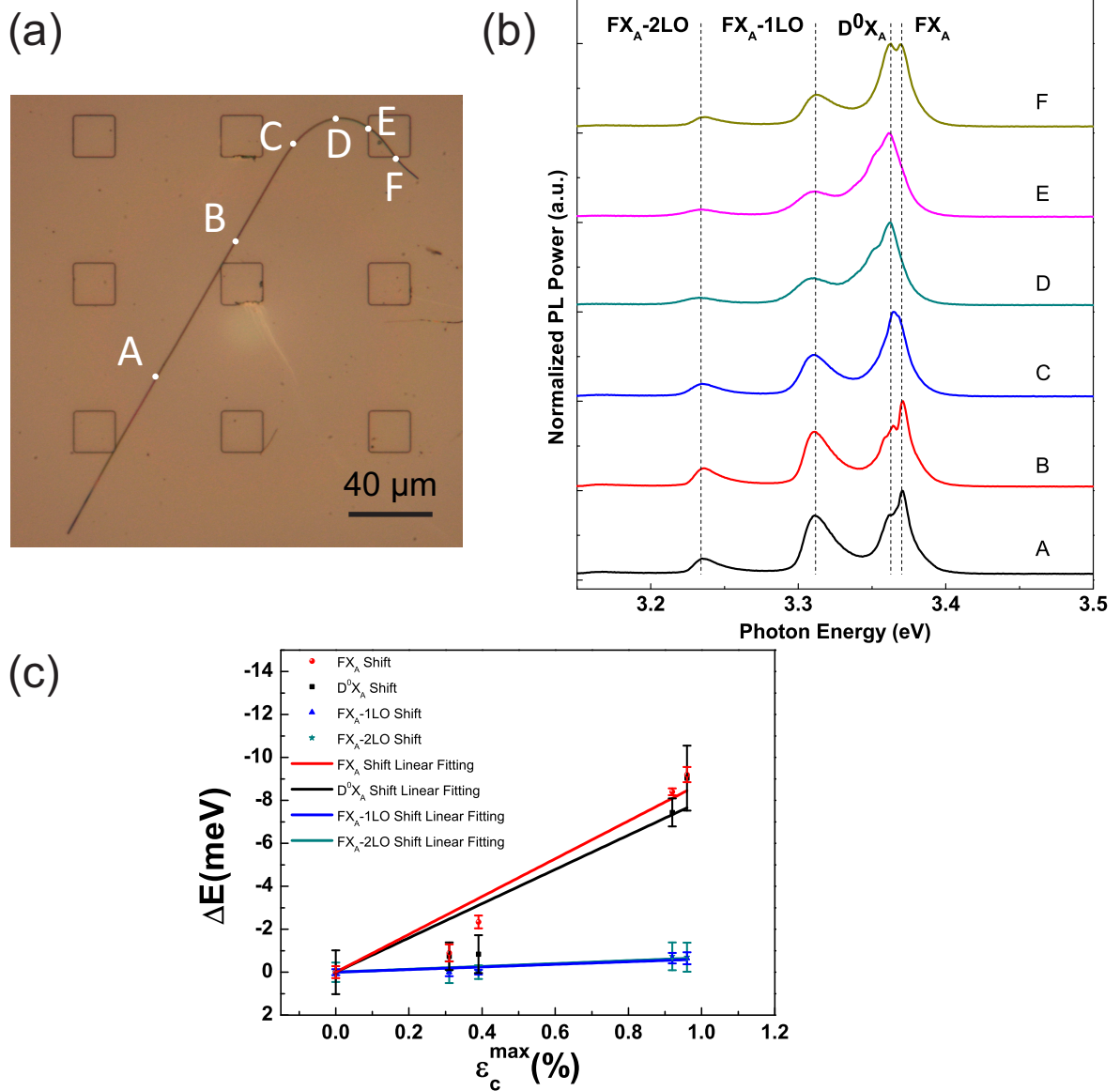


Figure S 1: A bent ZnO NW with a diameter of about 310 nm. (a) The optical image of the bent NW. (b) The corresponding PL spectra acquired from the positions indicated in (a). (c) Energy shifts of FX_A , D^0X_A , $\text{FX}_A - 1\text{LO}$ and $\text{FX}_A - 2\text{LO}$ versus local maximum strain. The solid lines are the linear fitting results.

2. Energy shift versus diameter of the NWs

If we do not consider the effect of surface potential, the $E_{c0}(x)$ in Eq. (2) is independent on the spatial coordinate. Then, we have:

$$E_c(x) = E_{c0} + \Delta E_c^{piezo}(x) + \Delta E_c^{deform}(x).$$

So, using Eqs. (1)-(5), the PL intensity is given by:

$$\begin{aligned} I(h\nu) &\propto \int n(x) f(h\nu - h\nu_c(x)) dx \\ &= \int n_c \exp\left(-\frac{E_{c0} - \frac{2b\epsilon_c^{max}x}{d_{NW}} + \frac{a_g\epsilon_c^{max}x}{d_{NW}}}{kT}\right) f\left(h\nu - E_g - \frac{2a_g\epsilon_c^{max}x}{d_{NW}}\right) dx \\ &= \frac{d_{NW}}{\epsilon_c^{max}} \int n_c \exp\left(-\frac{E_{c0} - 2bt + a_gt}{kT}\right) f(h\nu - E_g - 2a_gt) dt, \left(t = \frac{\epsilon_c^{max}x}{d_{NW}}\right) \\ &= \frac{d_{NW}}{\epsilon_c^{max}} I_t, \left(I_t = \int n_c \exp\left(-\frac{E_{c0} - 2bt + a_gt}{kT}\right) f(h\nu - E_g - 2a_gt) dt\right). \end{aligned}$$

Obviously, the part I_t is independent on the diameter d_{NW} . So, the position of PL peak is also independent on the d_{NW} . The diameter only affects the intensity of PL.

3. Raman spectroscopy

The wurtzite structure of ZnO belongs to the C_{6v}^4 space group. The group theory analysis predicts the zone center optical phonons are: $A_1 + 2B_1 + E_1 + 2E_2$. The A_1 , E_1 , and E_2 modes are Raman active, while the B_1 modes are forbidden. The polar A_1 and E_1 modes split into longitudinal optical (LO) and transverse optical (TO) components. From Figure S2, only E_2^{high} mode centered at $\sim 435.02 \text{ cm}^{-1}$ appears. The E_2^{high} mode is mainly due to the motion of oxygen atoms perpendicular to c-axis of ZnO. The strain along c-axis will cause bond bending and result in shift of E_2^{high} . In Figure S2, the tensile strain decreases the E_2^{high} phonon energy and results in redshift of the peak from 435.02 cm^{-1} to 434.86 cm^{-1} , while the compressive strain increases the E_2^{high} phonon energy

and results in blueshift of the peak from 435.02 cm^{-1} to 436.12 cm^{-1} .

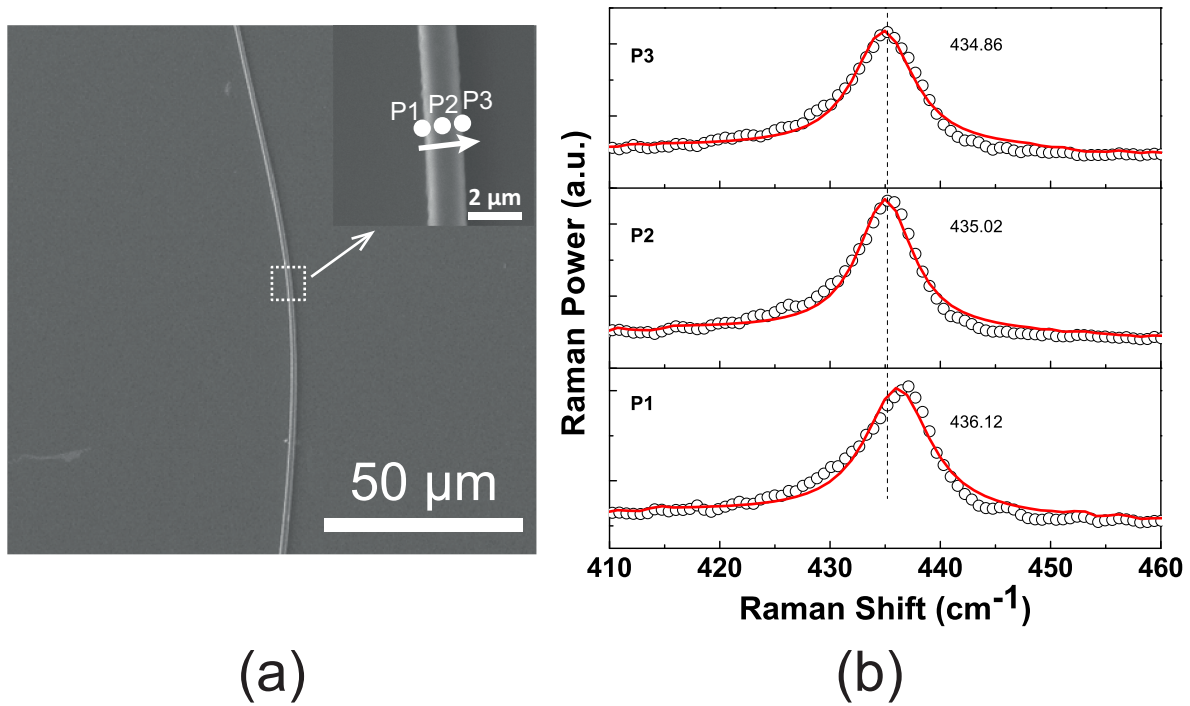


Figure S 2: Raman spectra acquired at different positions of a individual bent ZnO NW. (a) SEM image of the NW with a diameter of $\sim 1.5\text{ }\mu\text{m}$. The inset is the enlarged image at the bent region. (b) Raman spectra (open circles) acquired at three different positions along the radial direction of the NW. Red solid lines are the Lorentzian fittings to the experimental data. The corresponding values for the peak positions are indicated in the figure.