Electronic Supplementary Information

Effect of Hydrogen Chloride Etching on Carrier Recombination Processes of Indium Phosphide Nanowires

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1. Sample Preparation and Experimental design

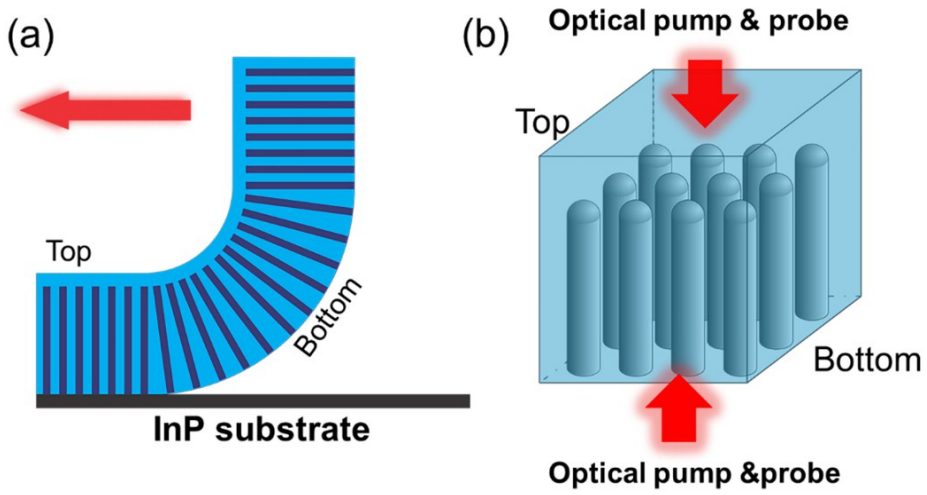

Fig. S1 (a) The method of the InP nanowire (NW) array peels off from the substrate. (b) The sketch of the NW samples used for TRPL and TRTS measurements.

After the InP nanowires (NWs) were grown on the InP (111)B substrates by the MOVPE method, we embedded the NWs in the colorless First Contact polymer film and then removed from the native substrate together with the polymer by a peel-off procedure (as shown in Fig. S1(a)). Here we define the side of the NW array that was next to the InP substrate of the as-grown samples are the bottom part and the opposite side as the top side. With these polymer-embedded InP NW arrays, we can excite the samples from the top and bottom side, as shown in Fig. S1 (b).

2. Photoluminescence (PL) spectra and decay time of as gown InP nanowire

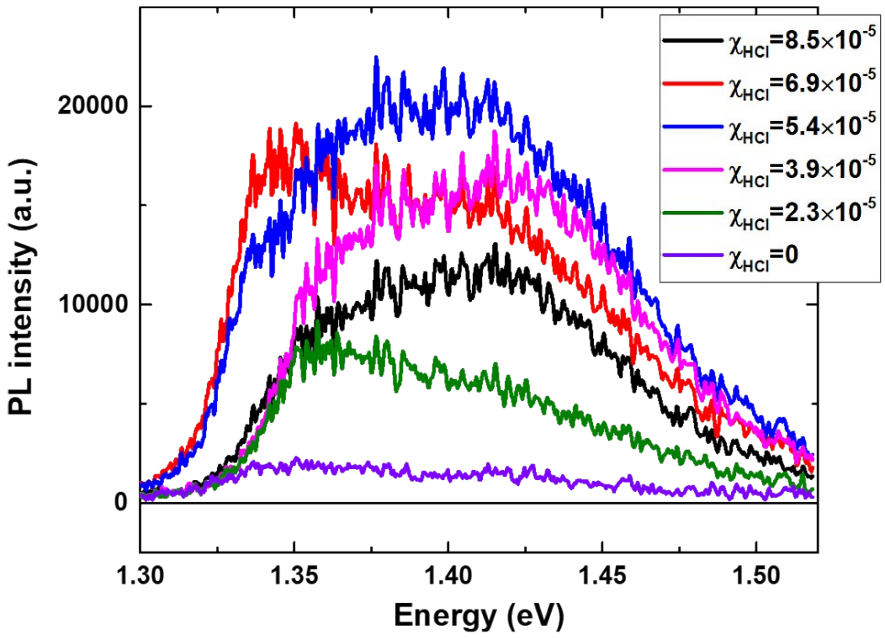

Fig. S2-1 PL spectra of the InP nanowires grow with different HCl molar fraction. The spectra were measured in focus mode. We found that the PL emission is band-edge emission (from wurtzite and zinc-blende parts of InP nanowires), and no emission from defects were observed. The relative PL intensity decay has a similar trend with the TRPL decay.

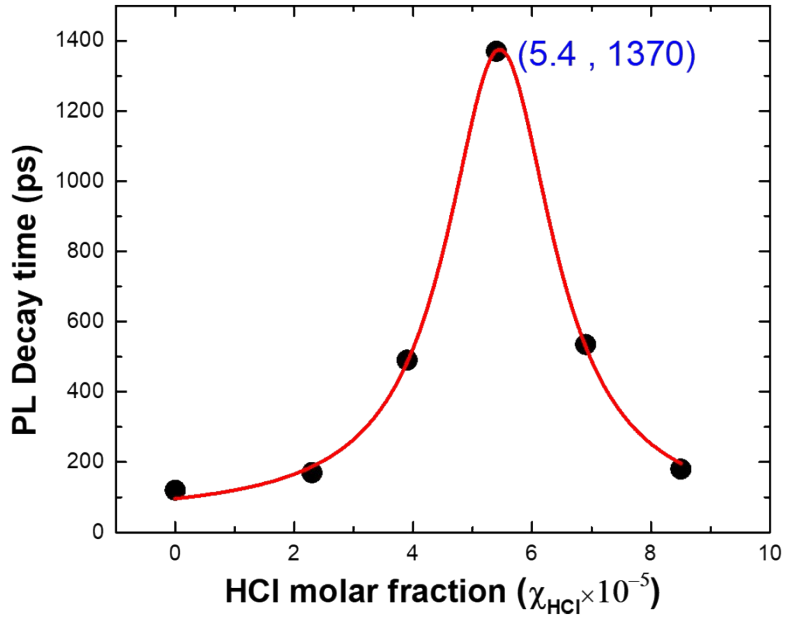

Fig. S2-2 The dependence of the PL decay time (τ_{PL}) on the HCl molar fractions (χ_{HCl}). The emission decay times were defined as the time it takes for the PL signal to reduce by *e* times from its initial value. The PL measurements were conducted at 400 nm excitation with the fluence of 9×10^{11} cm^{-2}. The fitted decay times were fitted by Lorentz function for a simple quantification. From the Lorenz fit, it appears that the $\chi_{HCl} = 5.4\times10^{-5}$ is very close to the largest passivation effect.

Table ST1 Fitting parameters of TRPL kinetics traces in Fig. 3(a).

Kinetics traces of TRPL		**Fitting parameters**			
Sample	**Fluence** (photons/cm^2 $pulse^1$)	A_1	τ_1 (ps)	A_2	τ_2 (ps)
$\chi_{HCl}=0$	9.0×10^{11}	0.82	60	0.18	550
$\chi_{HCl}=2.3\times10^{-5}$	9.0×10^{11}	0.70	80	0.30	500
$\chi_{HCl}=3.9\times10^{-5}$	9.0×10^{11}	0.57	130	0.43	1700
$\chi_{HCl}=5.4\times10^{-5}$	9.0×10^{11}	0.29	240	0.71	2000
$\chi_{HCl}=6.9\times10^{-5}$	9.0×10^{11}	0.53	120	0.47	1500
$\chi_{HCl}=8.5\times10^{-5}$	9.0×10^{11}	0.76	90	0.24	700

Table ST2 Fitting parameters of TRPL kinetics traces in Fig. 3(b).

Kinetics traces of TRPL			**Fitting parameters**			
Sample	**Fluence** (photons/cm^2 pulse^1)		A_1	τ_1 (ps)	A_2	τ_2 (ps)
χ_{HCl}=0	9×10^{11}	Bottom	0.46	140	0.54	560
		Top	0.73	80	0.27	480
χ_{HCl}=5.4×10^{-5}	9×10^{11}	Bottom	0.52	250	0.48	1000
		Top	0.33	140	0.67	900
χ_{HCl}=8.5×10^{-5}	9×10^{11}	Bottom	0.38	230	0.62	960
		Top	0.40	70	0.60	360

Table ST3 Fitting parameters of TRPL kinetics traces in Fig. 4.

Kinetics traces of TRPL		**Fitting parameters**			
Sample	**Fluence** (photons/cm^2 pulse^1)	A_1	τ_1 (ps)	A_2	τ_2 (ps)
χ_{HCl}=0	4.5×10^{11}	0.81	70	0.19	560
	9.0×10^{11}	0.82	60	0.18	530
χ_{HCl}=5.4×10^{-5}	4.5×10^{11}	0.01	830	0.99	1600
	9.0×10^{11}	0.30	260	0.70	2000
χ_{HCl}=8.5×10^{-5}	4.5×10^{11}	0.75	110	0.25	800
	9.0×10^{11}	0.77	100	0.23	720

3. Excitation fluence dependence of the photoconductivity kinetics of InP

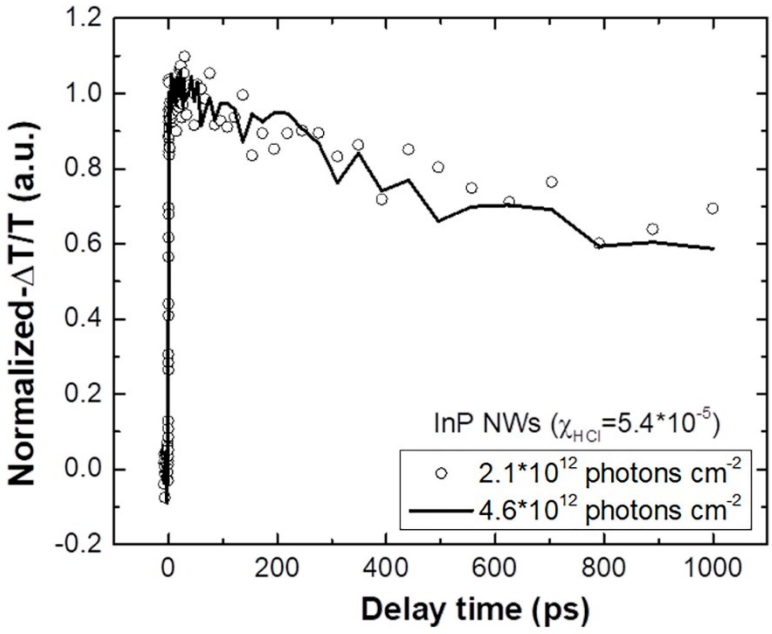

Fig. S3 Photoconductivity kinetics of InP NWs with HCl etching of $\chi_{HCl}=5.4\times10^{-5}$ under the indicated excitation densities. The excitation wavelength is 800 nm.

Table ST4 Fitting parameters of transient THz transmittance kinetics traces in Fig. 5(a).

Kinetics traces of TRTS		**Fitting parameters**			
Sample	**Fluence** (photons/cm^2 pulse^1)	A_1	τ_1 (ps)	A_2	τ_2 (ps)
$\chi_{HCl}=0$	4.6×10^{12}	0.49	570	0.51	11000
$\chi_{HCl}=5.4\times10^{-5}$	4.6×10^{12}	1.00	4400	-	-
$\chi_{HCl}=8.5\times10^{-5}$	4.6×10^{12}	0.08	870	0.92	1400

4. The photoconductivity kinetics of InP excited via different sides

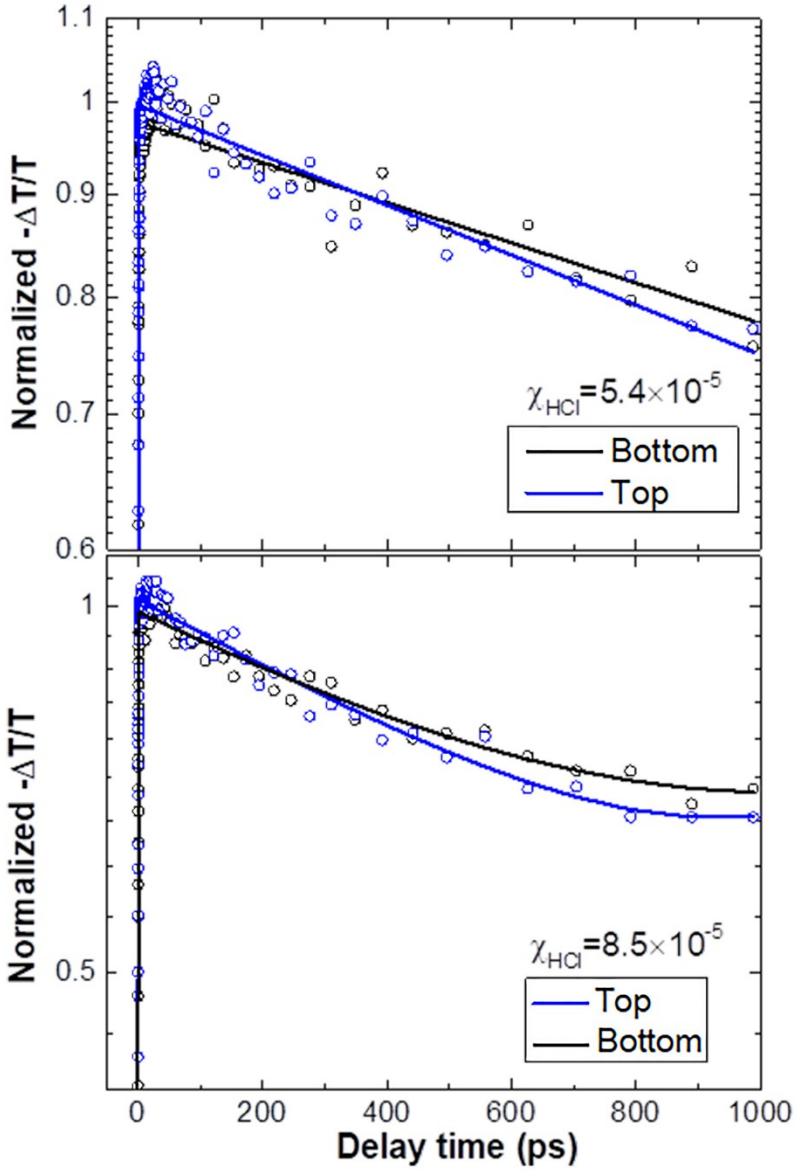

Fig. S4 Normalized transient THz transmittane kinetics of InP NWs with HCl etching of $\chi_{HCl}=5.4\times10^{-5}$ and 8.5×10^{-5} after photoexcitation via polymer side (Top) and NWs side (Bottom). The InP NWs are embedded in FC polymer. The excitation wavelength is 800 nm. The fitting parameters are given in Table ST5.

Table ST5 Fitting parameters of transient THz transmittance kinetics traces in Fig. S4 and Fig. 5(b).

Kinetics traces of TRTS			**Fitting parameters**			
Sample	**Fluence** (photons/cm^2 pulse^1)		A_1	τ_1 (ps)	A_2	τ_2 (ps)
χ_{HCl}=0	4.6×10^{12}	Bottom	0.49	570	0.51	11000
		Top	0.27	120	0.73	2900
$\chi_{HCl}=5.4\times10^{-5}$	4.6×10^{12}	Bottom	1.00	4400	-	-
		Top	1.00	3500	-	-
$\chi_{HCl}=8.5\times10^{-5}$	4.6×10^{12}	Bottom	0.08	870	0.92	1400
		Top	0.01	370	0.99	1500

5. Calculation of the carrier mobility in InP nanowires

This section outlines the extraction of the NW carrier mobility μ from the TRTS data. From SEM images of as grown InP NW arrays, we caculated the effective areal fill factor of NWs embedded in colorless First contact polymer (CFCP) withthin a layer thickness of d (2 μm), f, as 12.5% for all the InP NW arrays. For the calculations of the photoconductivity, we consider NWs of a length d embedded in CFCP, see Fig. S5.

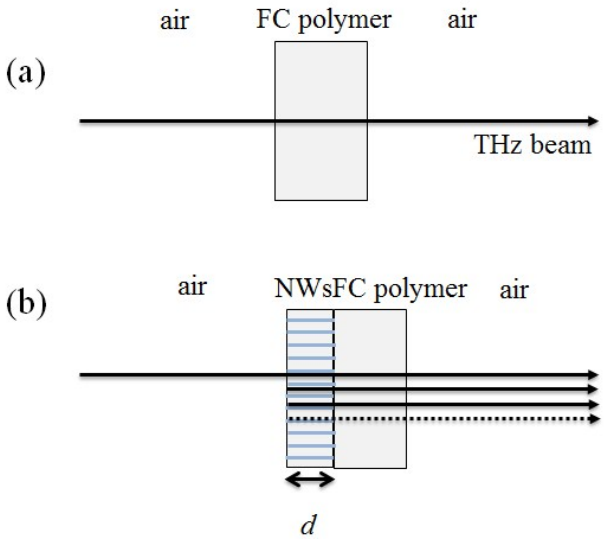

Fig. S5 The Optical path of the terahertz beam transmitted through CFCP (a) without and (b) with nanowires.

The transmitted terahertz electric fields with and without the optical pump are defined as:[1]

$$E_{\text{on}} = fE_{\text{NW}^*} + (1-f)E_{\text{P}} \tag{1}$$

$$E_{\text{off}} = fE_{\text{NW}} + (1-f)E_{\text{P}} \tag{2}$$

Where E_{NW} and E_P are terahertz transmissions through NWs and CFCP, respectively, and * indicates photoexcited state.

Combining Equations (1) and (2) gives:

$$\frac{\Delta E}{E} = \frac{E_{\text{on}} - E_{\text{off}}}{E_{\text{off}}} = \frac{\frac{E_{\text{NW}^*}}{E_{\text{NW}}} - 1}{1 + (1/f - 1)\frac{E_{\text{P}}}{E_{\text{NW}}}} \tag{3}$$

Where $\Delta E = E_{on} - E_{off}$; $E = E_{off}$.

From Equation (3), pump induced THz electric field change of NWs can be written as:

$$\frac{\Delta E_{\text{NW}}}{E_{\text{NW}}} = \frac{E_{\text{NW}^*} - E_{\text{NW}}}{E_{\text{NW}}} = \frac{\Delta E}{E}\left(1 + (1/f - 1)\frac{E_{\text{P}}}{E_{\text{NW}}}\right) \tag{4}$$

We find that terahertz transmissions through CFCP polymers with and without NW layer are similar. Thus, we can approximate the ratio of $E_P/E_{NW} \sim 1$. Then

$$\frac{\Delta E_{\text{NW}}}{E_{\text{NW}}} = \frac{E_{\text{NW}^*} - E_{\text{NW}}}{E_{\text{NW}}} \approx \frac{\Delta E}{E}\frac{1}{f} \tag{5}$$

Transient conductivity $\Delta\sigma$ is a product of mobility and concentration of photo-generated charge carriers. To evaluate electron mobility μ, we divide $\Delta\sigma$ by the number of photo-generated charge carriers eN_{exc}:[2-4]

$$\xi\mu = \frac{\Delta\sigma}{\text{e}N_{\text{exc}}} = -(n_1 + n_2)\varepsilon_0 c\frac{1}{eF}\frac{\Delta E_{\text{NW}}}{E_{\text{NW}}} = -(n_1 + n_2)\varepsilon_0 c\frac{1}{efF}\frac{\Delta E}{E} \tag{6}$$

where ξ is the quantum yield of charge photogeneration, μ is carrier mobility, n_1 and n_2 are refractive indices of the air and CFCP respectively, F is the fluence in photons per cm^2 and $\Delta E_{NW}/E_{NW}$ is the transmitted terahertz electric field change in the NW in CFCP. We assume that at the earliest time scales (t < 3 ps), ξ = 1, as all absorbed photons are converted to mobile charges.[5] Hence, we can estimate carrier mobility by the equation (6) and obtain 2200 cm^2 V^{-1} s^{-1} for InP NWs at the fluence of 2.3×10^{11} photons/cm^2.

6. Comparison of TRPL, TRTS and TA in the InP nanowires

As shown in the article (Fig. 7(a)) and in the Fig. S6, the TA decay is slightly slower than THz signal decay, whereas the TRPL decay is obviously the fastest. We observed that the TA decay is close to the TRTS decay in the InP NWs with HCl etching of $\chi_{HCl}=8.5\times10^{-5}$, and it is slightly slower than TRTS decay in the NWs without HCl etching. It is important to note though that the TA decay rate is dependent on the excitation density and in general become slower with a decrease of the excitation density. We found that in the similar excitation density range the TA decay is similar to or slower than TRTS decay.

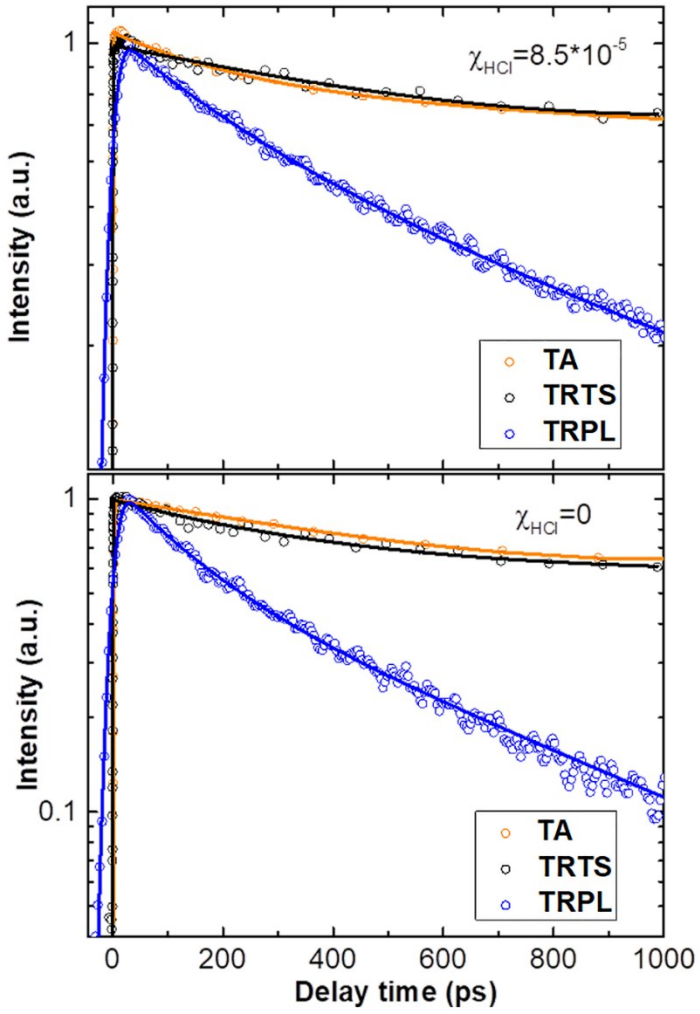

Fig. S6 Comparison of TRTS, TRPL and TA (all normalized to the peak value) in InP NWs with HCl etching of $\chi_{HCl}=8.5\times10^{-5}$ and 0. Solid lines are fitting curves based on mono-exponential decay functions.

Table ST6 Fitting parameters of the kinetics traces in Fig. S6 and Fig. 7(a).

Sample	**Techniques**	**Fluence** (photons/cm^2 pulse^1)	**Fitting parameters**					
			A_1	τ_1 (ps)	A_2	τ_2 (ps)	A_3	τ_3 (ps)
χ_{HCl}=0	TA	7.4×10^{12}	-0.04	580	0.65	2	0.96	1300
	TRPL	9×10^{11}	0.46	140	0.54	560	-	-
	TRTS	4.6×10^{12}	0.49	570	0.51	11000	-	-
$\chi_{HCl}=5.4\times10^{-5}$	TA	5.85×10^{11}	-0.56	1	-0.43	13	1.00	29000
	TRPL	9×10^{11}	0.52	250	0.48	1000	-	-
	TRTS	4.6×10^{12}	1.00	4400	-	-	-	-
$\chi_{HCl}=8.5\times10^{-5}$	TA	2.3×10^{13}	-0.68	1	0.28	240	0.76	8300
	TRPL	9×10^{11}	0.38	230	0.62	960	-	-
	TRTS	4.6×10^{12}	0.08	870	0.92	1400	-	-

7. TEM Images of InP nanowires

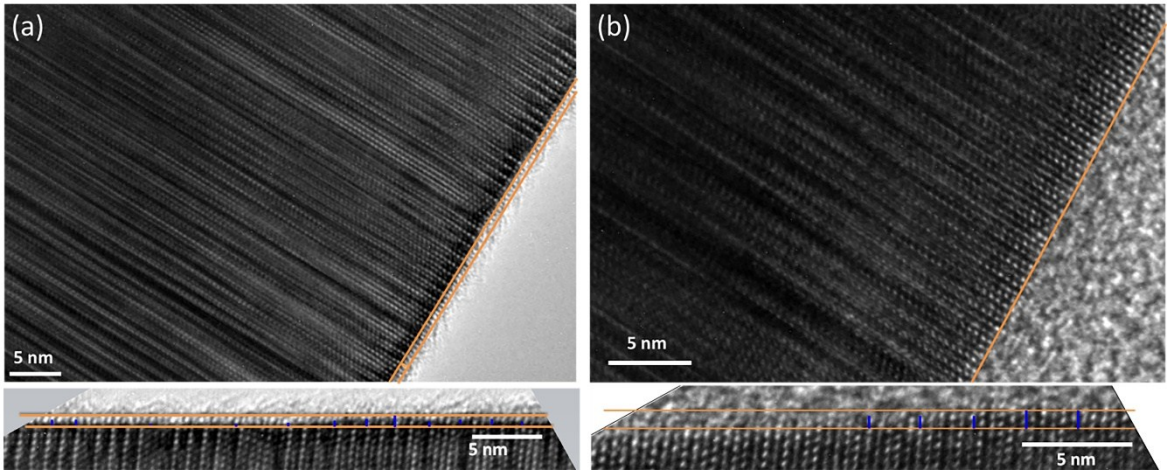

Fig. S7-1 HR-TEM images of top (a) and bottom (b) of the InP NW with HCl etching of $\chi_{HCl}=5.4\times10^{-5}$ during the growth.

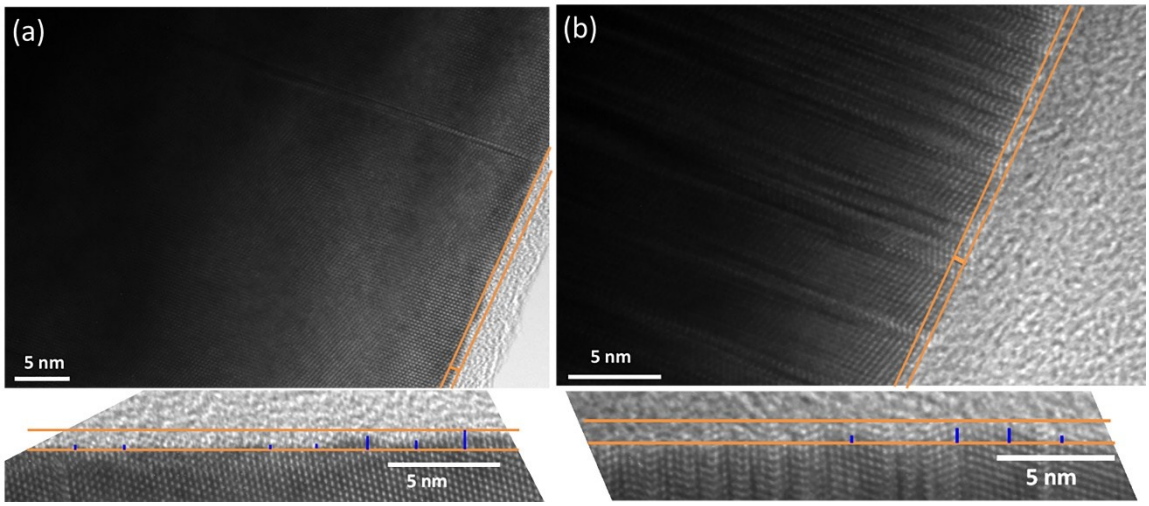

Fig. S7-2 HR-TEM images of top (a) and bottom (b) of the InP NW with HCl etching of $\chi_{HCl}=8.5\times10^{-5}$ during the growth.

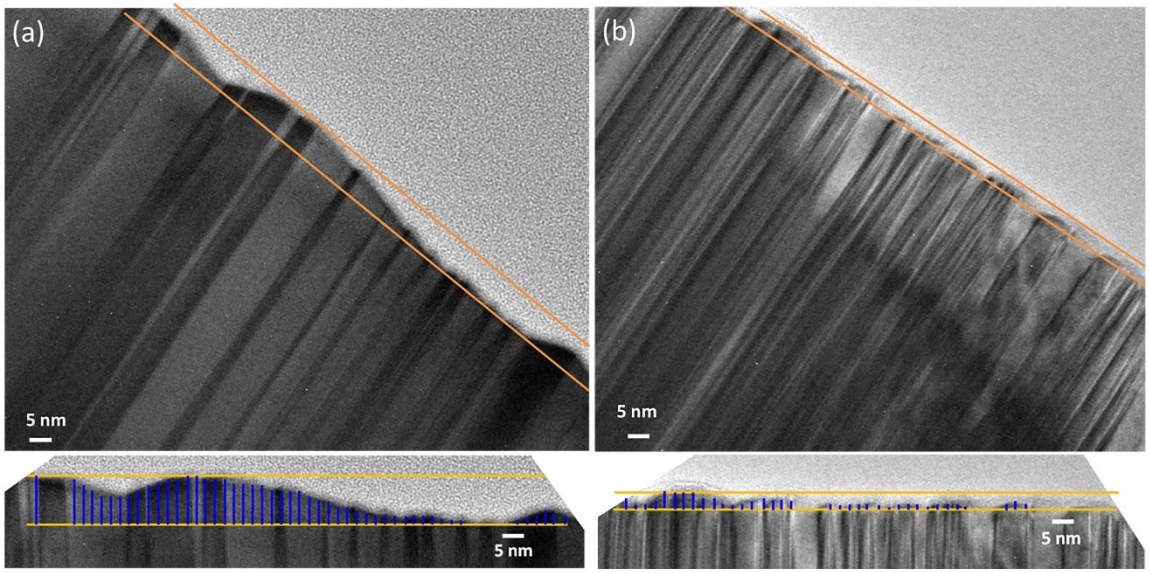

Fig. S7-3 HR-TEM images of top (a) and bottom (b) of the InP NW without HCl etching during the growth.

Stacking fault densities of the InP NW with different HCl etching during their growth were estimated from the TEM images and presented in Table ST7. Apparently, the stacking fault density on the top of the NW is lower than that on the bottom of the NW. We defined roughness of the NW as the mean deviation (*Ra*) of the assessed line (shown in Fig. S7, the orange line is the assessed line). As shown in Fig. S7-1~3, we take the same step (about 2.2nm) and measure the deviation of the assessed line. We can estimate the roughness from the TEM images as shown in Table ST7.

Table ST7 The stacking faults and roughness estimated from the HR-TEM.

HCl molar fraction χ_{HCl} ($\times 10^{-5}$)		0		5.4		8.5	
		Top	Bottom	Top	Bottom	Top	Bottom
Stacking fault (/μm)		105	133	96	350	56	371
Roughness	*L* (nm)	125	116	37.6	24.1	21.9	22.4
	Step (nm)	2.2	2.2	2.2	2.2	2.2	2.2
	Ra (nm)	5.77	1.23	0.25	0.28	0.28	0.21

8. The SAED patterns of the InP nanowires

The SAED patterns (or fast Fourier transform (FFT) results) of InP nanowires grown with HCl molar fraction of 0, 5.4×10^{-5}, and 8.5×10^{-5} are shown in Fig. S8. We clearly see that the nanowires are of crystalline as described in the discussion session of our paper. More detailed analysis of the nanowire crystallinity has been provided in the previous paper dedicated to the characterization of nanowires grown under different HCl etching conditions, see Ref. 6.

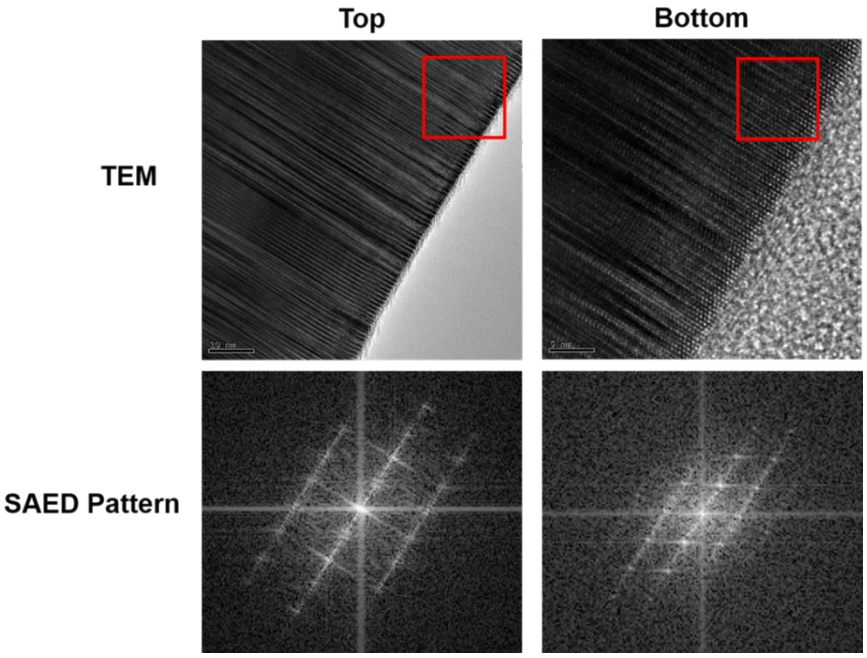

Fig. S8-1 HR-TEM images and the corresponding SAED pattern of the top and bottom of the InP NWs with HCl etching of $\chi_{HCl}=5.4\times10^{-5}$ during the growth. The square in red is the area of making fast Fourier transform.

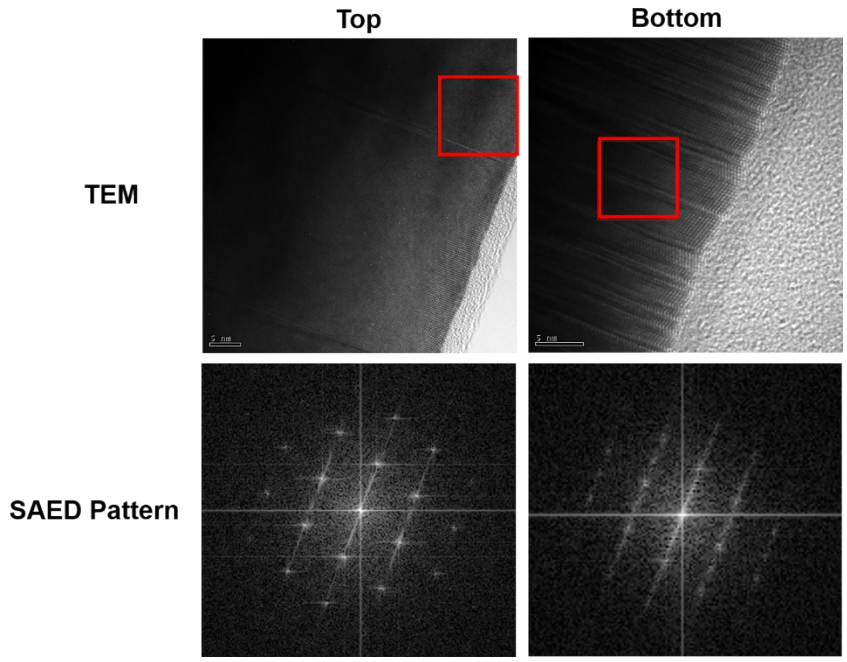

Fig. S8-2 HR-TEM images and the corresponding SAED pattern of the top and bottom of the InP NWs with HCl etching of $\chi_{HCl}=8.5\times10^{-5}$ during the growth. The square in red is the area of making fast Fourier transform.

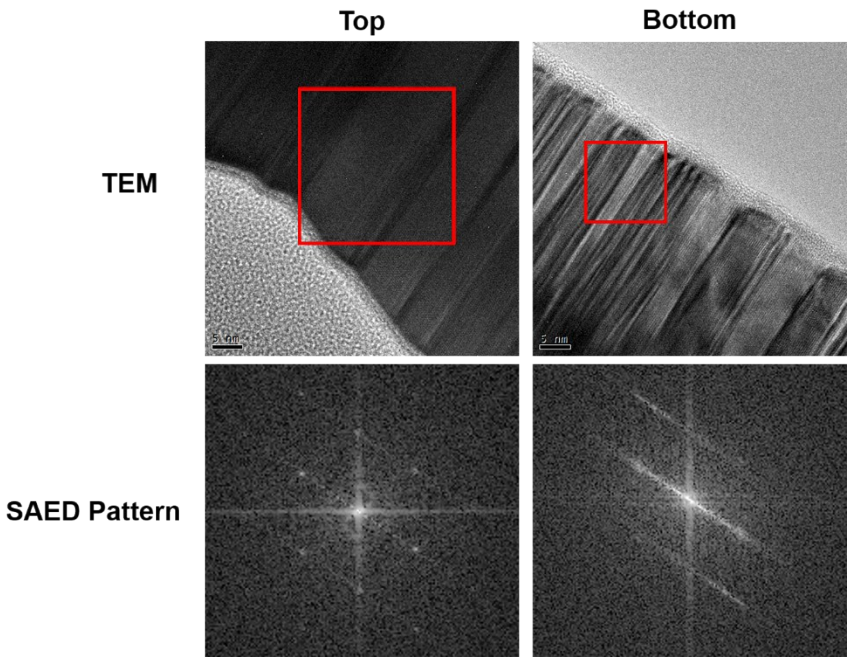

Fig. S8-3 HR-TEM images and the corresponding SAED pattern of the top and bottom of the InP NWs without HCl etching during the growth. The square in red is the area of making fast Fourier transform.

References

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