

Supplementary Information

Weight and Surface Area Estimations of TiO₂-NT/(Zn,Sn)Pd-ND and P25

(1) Weight of TiO₂-NT/(Zn,Sn)Pd-ND (1 cm² sample)

$$= \frac{\text{total weight with Ti substrate} - \text{weight of Ti substrate}}{\text{large sample size (total area)}} = \frac{0.5773 - 0.5655}{9.6} = 10^{-3} \text{ g}$$

(2) TiO₂ NT inner diameter $d \sim 190$ nm, outer diameter $D \sim 250$ nm, height $H \sim 500$ nm

$$\text{Inner surface area of each TiO}_2 \text{ NT} = 2\pi \left(\frac{d}{2} \right) \times H = 3.0 \times 10^{-9} \text{ cm}^2$$

$$\text{Outer surface area of each TiO}_2 \text{ NT} = 2\pi \left(\frac{D}{2} \right) \times H = 3.9 \times 10^{-9} \text{ cm}^2$$

$$\text{Number density of TiO}_2 \text{ NTs} \sim \frac{14}{1.1 \times 10^6} \text{ NT/nm}^2 = 1.3 \times 10^9 \text{ NT/cm}^2$$

$$\text{Total surface area of TiO}_2 \text{ NTs (1 cm}^2 \text{ sample}) = (6.9 \times 10^{-9}) \times (1.3 \times 10^9) = 9.0 \text{ cm}^2$$

(3) Size of P25 NPs $S \sim 25$ nm, gravity density $G \sim 4.0 \text{ g/cm}^3$

$$\text{Surface area of each P25 NP} = 4\pi \left(\frac{S}{2} \right)^2 = 4\pi \left(\frac{25}{2} \right)^2 = 2.0 \times 10^{-11} \text{ cm}^2$$

$$\text{Weight of each P25 NP} = \frac{4\pi}{3} \left(\frac{S}{2} \right)^3 \times G = \frac{4\pi}{3} \left(\frac{25}{2} \right)^3 \times 4.0 = 3.3 \times 10^{-17} \text{ g}$$

$$\text{Number of P25 NPs (10}^{-3} \text{ g sample}) = \frac{10^{-3}}{3.3 \times 10^{-17}} = 3.0 \times 10^{13}$$

$$\text{Total surface area of P25 NPs (10}^{-3} \text{ g sample}) = (2.0 \times 10^{-11}) \times (3.0 \times 10^{13}) = 6.0 \times 10^2 \text{ cm}^2$$

Bonding Configuration and Composition Analyses of TiO₂-NT/(Zn,Sn)Pd-ND

Table S1. XPS binding energies and full widths at half maximum (FWHMs) of Pd_{3d}, Sn_{3d}, Zn_{2p} and Ti_{2p} peaks and the compositions of (Zn,Sn)Pd NDs on TiO₂ NTs.

Peak	Binding Energy (eV)		FWHM (eV)		Area	R.S.F. [†]	Area/ R.S.F.	Content (at.%)	Content (at.%) [*]
	Reference	Present	Reference	Present					
Pd 3d5/2	335.5 [1]	335.6	1.25 [2]	1.15	72457	1182.677	61.27	72.21	81.30
Pd 3d3/2	340.8 [3]	340.9	1.10 [4]	1.20					
Sn 3d5/2	485.1 [5]	485.3	1.00 [6]	1.10	1234	1716.800	0.72	0.85	0.95
Sn 3d3/2	493.5 [6]	493.7	1.80 [8]	1.80					
Sn 3d5/2-SnO ₂	487.1 [7]	487.1	1.40 [6]	1.40	3752	1716.800	2.19	2.58	
Sn 3d3/2-SnO ₂	495.5 [6]	495.5	1.45 [8]	1.50					
Zn 2p3/2	1022.0 [9]	1022.1	2.00 [9]	2.00	11445	855.945	13.37	15.76	17.74
Zn 2p1/2	1045.1 [9]	1045.1	1.95 [9]	2.05					
Ti 2p3/2-TiO ₂	459.3 [10]	459.3	1.20 [11]	1.20	3093	423.679	7.30	8.60	
Ti 2p1/2-TiO ₂	465.1 [10]	465.1	1.20 [12]	1.50					

[†] Relative sensitivity factor; * contents without considerations of SnO₂ and TiO₂. Note: Auger spectrum of Zn LMM present in the XPS Sn_{3d3/2} spectrum in Figure 4 is considered during bonding configuration analyses and excluded from the composition analyses of Sn.

Growth Orientation Examinations of (Zn,Sn)Pd NDs

From the standard interplanar spacing (d) and angles of fcc Pd (JCPDS No. 46-1043) listed in Supplemental **Table S2**, and the standard SAD pattern of fcc Pd (zone axis [$\bar{1}01$])) plotted in Supplemental **Figure S1**, the growth orientations of (Zn,Sn)Pd NDs in different regions of **Figure 4** were determined as given in Supplemental **Figure S2** as:

R1: measured $d_{111} = 0.224$ nm, angle to primary arm = $70^\circ \rightarrow$ growth direction: [111];

R2: measured $d_{111} = 0.224$ nm, angle to branch = 70° ; measured $d_{101} = 0.260$ nm, angle to branch = $35^\circ \rightarrow$ growth direction: [111];

R3: measured $d_{101} = 0.260$ nm, angle to primary arm = $35^\circ \rightarrow$ growth direction: [111];

R4: measured $d_{010} = 0.390$ nm, angle to branch = $55^\circ \rightarrow$ growth direction: [111].

Table S2. Standard interplanar spacing (d) and angles of fcc Pd (JCPDS No. 46-1043).

Plane	{100}	{110}	{111}
d (nm)	0.3890	0.2751	0.2246
{100}	90.0°		
{110}	45.0°	60.0°	
{111}	54.7°	35.3°	70.5°

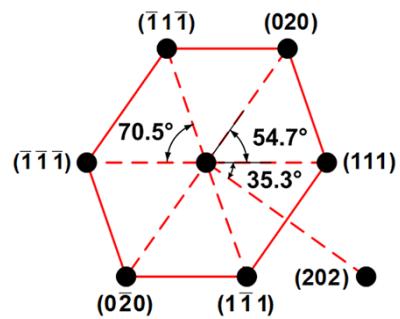


Figure S1. Standard SAD pattern of fcc Pd (zone axis $[101]$).

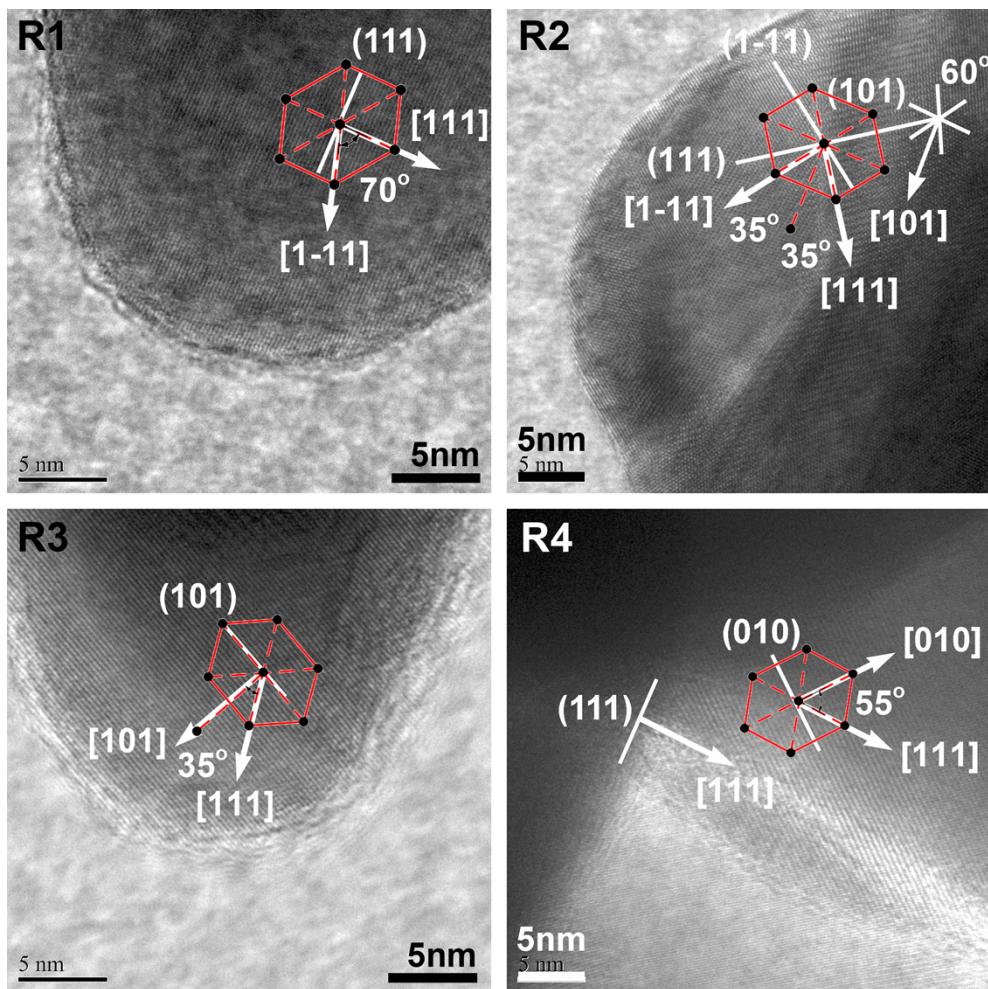


Figure S2. High-resolution TEM images and corresponding standard SAD patterns (zone axis $[101]$) showing the growth orientations of (Zn,Sn)Pd NDs in different regions of Figure 4 (R1, R2, R3, R4) all along $<111>$ direction group.

References

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