**Supporting Information**

Structural Control of PtNi Catalysts through Precise Synthesis Conditions and Elucidation of Property Determinants by *operando* XAS Analysis

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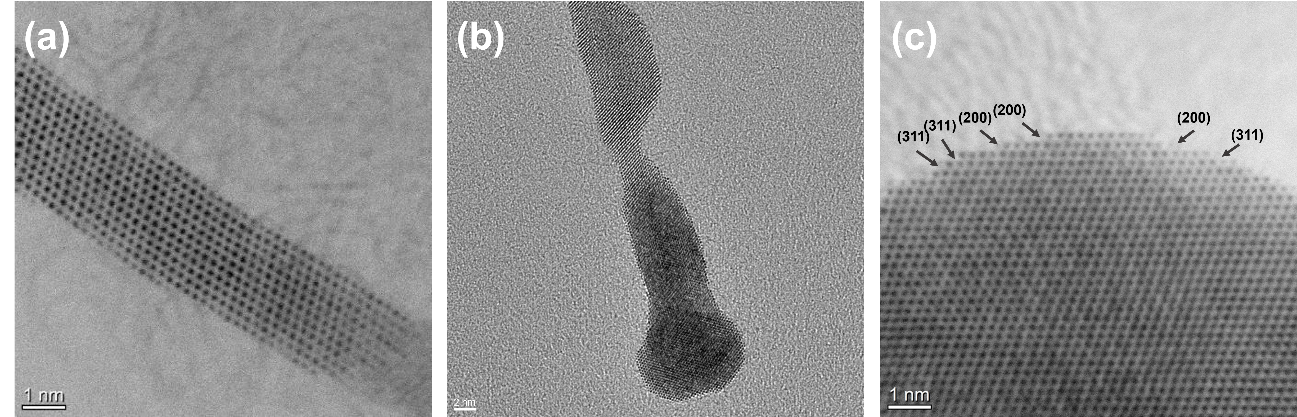
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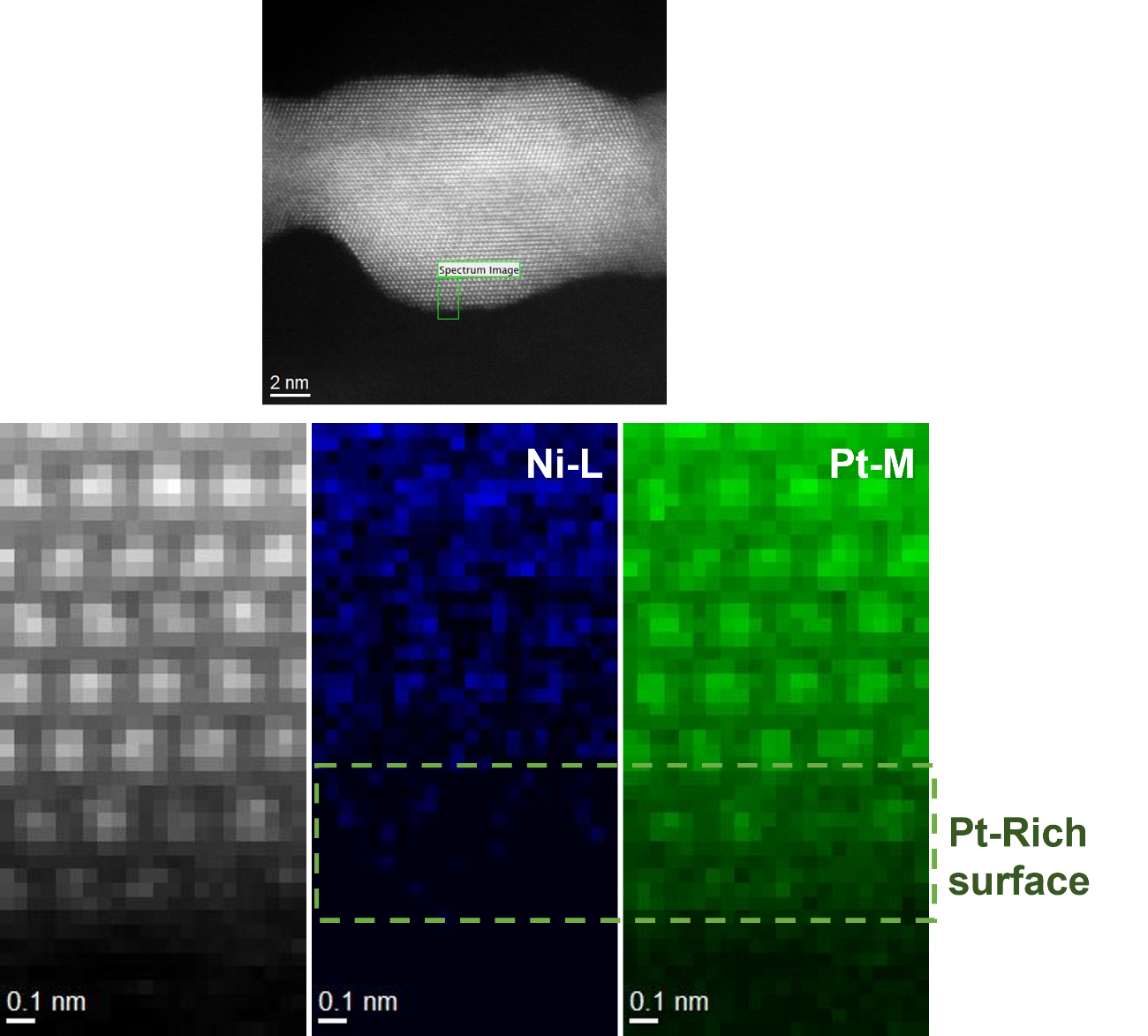
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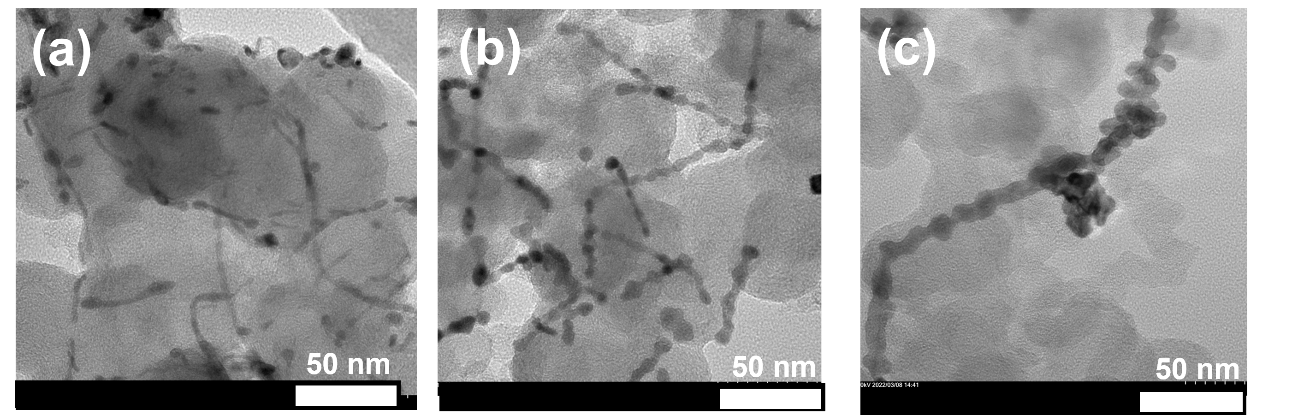
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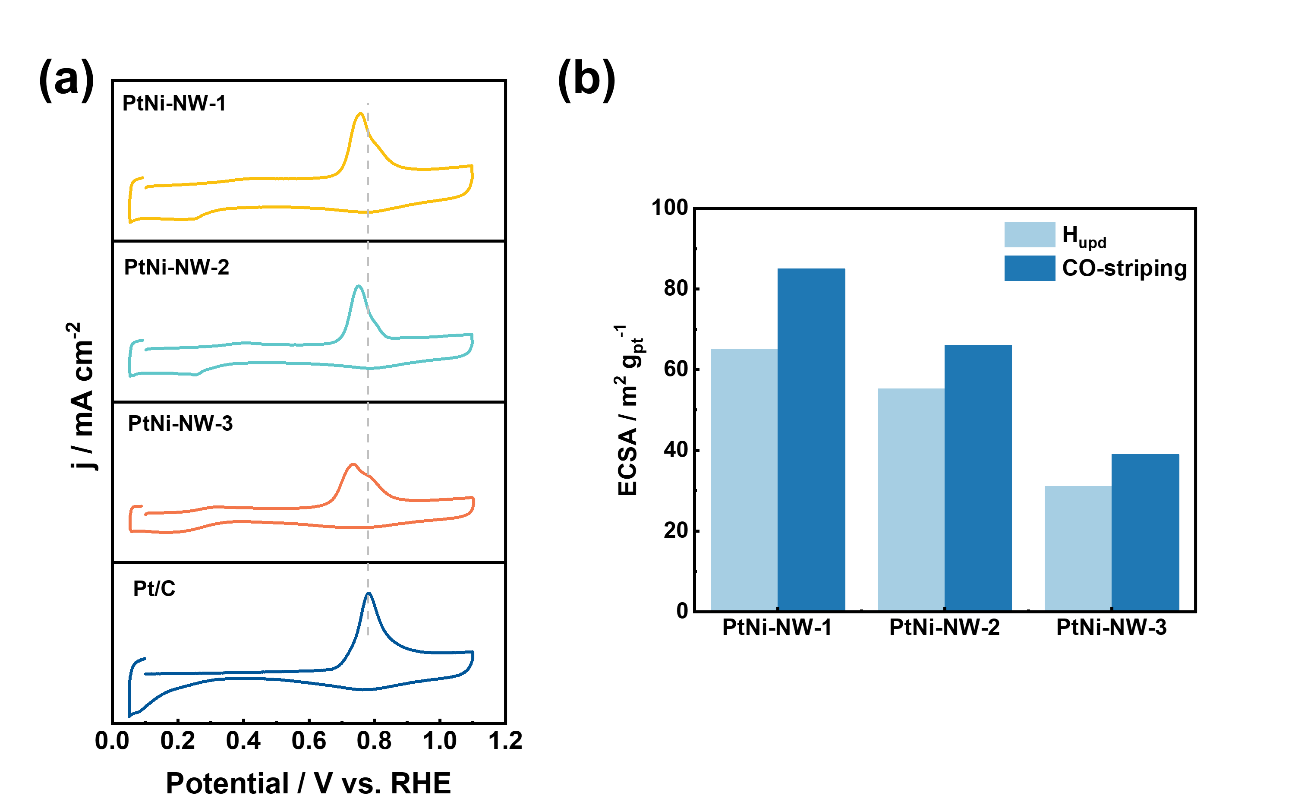
**Figure S1.** STEM image of (a) PtNi-NW-1, (b) PtNi-NW-2 and (c) PtNi-NW-3.



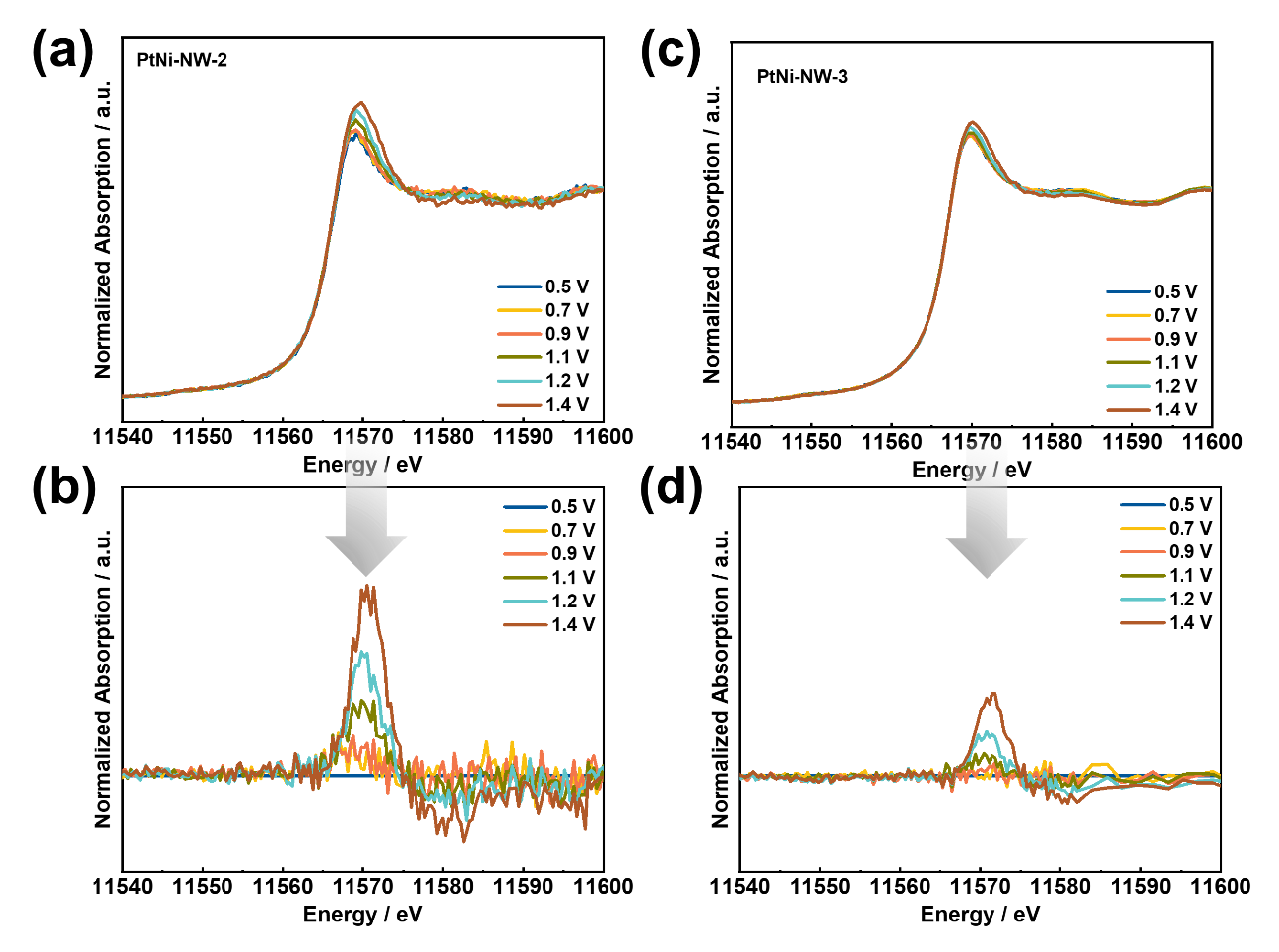
**Figure S2.** STEM-EELS mappings for PtNi-NW-3.



**Figure S3.** TEM image of (a) PtNi-NW-1, (c) PtNi-NW-2 and (c) PtNi-NW-3 after 400 ℃ H2/N2 annealing treatment.



**Figure S4.** (a) The CO-stripping curves of PtNi-NW-1, PtNi-NW-2, PtNi-NW-3 and Pt /C. (b) ECSA comparison of three catalysts.



**Figure S5.** Pt L3-edge XANES spectra of (a, b) PtNi-NW-2 and (c, d) PtNi-NW-3

**Table S1.** Acidic ORR activity and durability of PtNi-NW/C and state-of-the-art Pt-based nanocatalysts from recent years-published work.

|  |  |  |  |
| --- | --- | --- | --- |
| Catalysts | Mass activity at 0.9 V (A mgPt-1) | Specific activity at 0.9 V (mA cmPt-2) | References |
|
| IMC-PtFeMo/C nanowire | 2.56 | 5.41 | *Nano Energy*, 2024, **129**, 110079 |
| PtNi/C nanowire | 0.28 | 0.25 | *ACS Catal.,* 2024, **14**, 1750–1758 |
| PtNi NW/C | 1.85 | 1.64 | *Chin. Chem. Lett.,* 2024, **35**, 108445 |
| PtNiGa NW/C | 2.37 | 1.89 |
| Pt2Ni1/C nanowire | 0.095 | 0.24 | *Int. J. Hydrogen Energy.,* 2024, **51**, 1487 |
| L12-Pt3Co/C nanowire | 0.31 | 2.47 | *Adv. Funct. Mater.,* 2024, **34**, 2311618. |
| A1-Pt3Co/C nanowire | 0.12 | 1.1 |
| Pt@Pt-skin Pt3Ni nanowire | 6.69 | 8.42 | *Nat. Commun.*, 2023, **14**, 1518 |
| Pt–Ni Nanochains | 1.78 | 3.11 | *Adv. Mater.*, 2023, **35**, 2206508 |
| Pt–Ni Nanowires | 1.25 | 2.92 |
| Pt-Ni Bunched-Nanocages | 1.95 | 3.55 | *Adv. Energy Mater.* 2023, **13**, 2204257. |
| PtNiCo branched  nanocages | 1.03 | 2.75 | *J. Mater. Chem. A*, 2021,**9**, 23444 |
| PtNi branched  nanocages | 0.37 | 1.39 |
| Jagged Pt nanowires/C | 13.6 | 11.5 | *Science*, 2016, **354**,1414 |
| Pt3Ni nanowires/C | 0.546 | 0.9 | *ACS Catal.*, 2019, **9**, 4488 |
| Re-PtNiGa tetrametallic NWs/C | 3.49 | 3.17 | *Appl. Catal. B: Environ.*, 2022, **303**, 120918 |
| PtNi NWs/C | 2.11 | 2.40 |
| WOx-(0.25)-PtNi NWs/C | 0.85 | 1.29 | *J. Colloid Interface Sci.*, 2022, **607**, 1928 |
| PtNi NWs/C | 0.33 | 0.60 |
| Pt/W0.02–SnO2–C | 0.23 | 0.37 | *J. Mater. Chem. A*, 2024,**12**,10799 |
| **PtNi-NW-3** | **1.06** | **2.73** | **This work** |

Ni FCC

**Table S2.** The corresponding R space curve fitting results of Pt L3-edge for the PtNi-NW-2 catalysts varying different potential. Fitting details: S02 was fixed at 0.90, which was obtained by fitting the reference foils. Fits were undergone in R-space for 1.5≤R≤3.3 Å, and the k1,2,3 weighting for Δk = 3 – 11 Å-1. The path of the Pt-Pt is from the crystal structure of fcc PtNi phase (*fm-3m*).

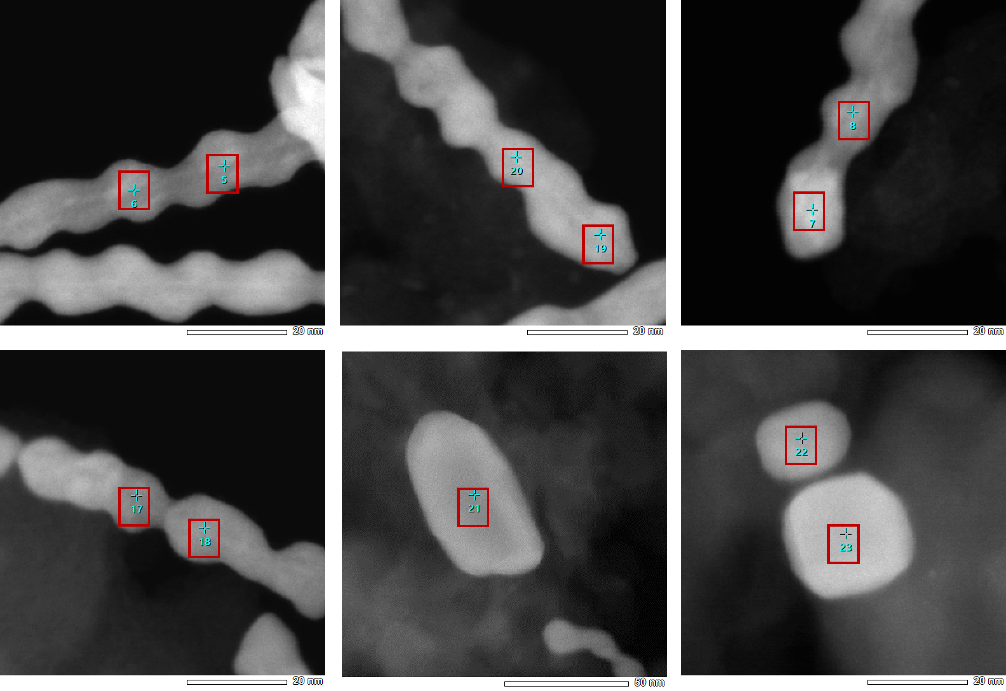
|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | Bond | Length/Å | CN | Debye−Waller factor | R-factor |
| 0.5 V | Pt-Pt | 2.686(5) | 8.9(1) | 0.004 | 0.3% |
| 0.7 V | Pt-Pt | 2.683(4) | 9.0(3) | 0.004 | 0.2% |
| 0.9 V | Pt-Pt | 2.690(5) | 8.8(3) | 0.005 | 1.1% |
| 1.1 V | Pt-Pt | 2.696(3) | 8.1(6) | 0.008 | 1.0% |
|  | Pt-O | 2.111(3) | 0.8(7) | 0.002 |
| 1.4 V | Pt-Pt | 2.722(6) | 6.6(2) | 0.002 | 2.0% |
|  | Pt-O | 2.110(2) | 2.6(2) | 0.003 |

**Table S3.** The corresponding R space curve fitting results of Pt L3-edge for the PtNi-NW-3 catalysts varying different potential.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | Bond | Length/Å | CN | Debye−Waller factor | R-factor |
| 0.5 V | Pt-Pt | 2.681(2) | 8.0(1) | 0.002 | 0.6% |
| 0.7 V | Pt-Pt | 2.683(2) | 8.2(3) | 0.008 | 0.3% |
| 0.9 V | Pt-Pt | 2.683(3) | 8.0(3) | 0.005 | 0.2% |
| 1.1 V | Pt-Pt | 2.685(4) | 7.7(6) | 0.003 | 1.3% |
|  | Pt-O | 2.113(3) | 0.3(1) | 0.007 |
| 1.4 V | Pt-Pt | 2.709(9) | 7.4(4) | 0.004 | 1.2% |
|  | Pt-O | 2.110(2) | 1.0(3) | 0.004 |

**Note 1:**

Several small nanoparticles appear during the synthesis process. To address this and ensure the representativeness of our data, we carefully considered the presence of these nanoparticles during the STEM-EDS analysis. Position and semi-quantitative analysis methods were employed. For instance, as shown in Fig. S6 and Table S4, we performed EDS analysis at 24 different positions on PtNi-NW-3, including both nanowire structures and nanoparticles.



**Figure S6.** STEM image of PtNi-NW-3 and examples of EDS analysis regions.

**Table S4**. Elemental content by position

|  |  |  |  |
| --- | --- | --- | --- |
| Quantitative analysis (at%) | | | |
| Position | Ni-K | Pt-L |
| 1 | 51.5 | 48.5 |
| 2 | 51.5 | 48.5 |
| 3 | 46.4 | 53.6 |
| 4 | 48.2 | 51.8 |
| 5 | 47.8 | 52.2 |
| 6 | 48.8 | 51.2 |
| 7 | 50.8 | 49.2 |
| 8 | 52.0 | 48.0 |
| 9 | 48.2 | 51.8 |
| 10 | 51.6 | 48.4 |
| 11 | 51.8 | 48.2 |
| 12 | 50.3 | 49.7 |
| 13 | 46.1 | 53.9 |
| 14 | 53.9 | 46.1 |
| 15 | 52.1 | 47.9 |
| 16 | 50.7 | 49.3 |
| 17 | 57.7 | 42.3 |
| 18 | 55.5 | 44.5 |
| 19 | 46.0 | 54.0 |
| 20 | 44.3 | 55.7 |
| 21 | 47.4 | 52.6 |
| 22 | 57.6 | 42.4 |
| 23 | 46.3 | 53.7 |
| **Average** | **50.3** | **49.7** |

**Note 2:**

The crystalline domain size (𝐷) was estimated using the Scherrer equation:

(1)

=0.9 (Scherrer constant),

=0.15418 (X-ray wavelength),

= FWHM of the (111) facet,

=41°（Bragg diffraction angle ).

The calculated grain sizes are summarized as PtNi-NW-1 (1.16 nm) < PtNi-NW-2 (1.22 nm) < PtNi-NW-3 (1.38 nm). This trend aligns with TEM observations and suggests that the increase in grain size correlates with enhanced surface roughness and high-index facet exposure

**Limitations of the Scherrer Equation for Nanowires**

While the Scherrer equation is a widely used method for estimating the crystalline domain size of nanoparticles, it has inherent limitations when applied to anisotropic materials such as nanowires. Unlike spherical particles, nanowires exhibit irregular morphology, surface roughness, a high number of exposed crystal facets, and potential amorphous regions, all of which can broaden XRD diffraction peaks and lead to an underestimation of the actual physical size observed via TEM.1

The Scherrer constant () is shape-dependent, with typical values ranging from 0.8 to 1.0 for spherical or isotropic particles. However, for nanowires, defining an accurate value is challenging due to their complex structural and surface characteristics. While some studies have discussed this issue, determining a precise value lies beyond the scope of this research.2 This limitation contributes to the discrepancy between the XRD-estimated grain size and the physical dimensions observed by TEM.

**Reference**

1. B. E. Warren, Phys. Rev., 59, 693-698 (1941).

2. D. J. Lim, N. A. Marks and M. R. Rowles, Carbon, 162, 475-480 (2020).