**Electronic Supplementary Information**

# Twinning boundary-elongated hierarchical Pt dendrites with an axially twinned nanorod core for excellent catalytic activity

Nguyen Tien Khi,[a] Jisun Yoon,[a] Hionsuck Baik,[b] Sangmin Lee,[c] Dongjune Ahn,[d] Seong Jung Kwon,[c*] Kwangyeol Lee[a*]

[a]Department of Chemistry and Research Institute for Natural Sciences, Korea University, Seoul 136-701 (Korea)

[c]Department of Chemistry, Konkuk University, Seoul 143-701 (Korea)

[b]Korea Basic Science Institute (KBSI), Seoul 136-713 (Korea)

[d] Department of Chemical and Biological Engineering, Korea University, Seoul 136-701 (Korea).

* Corresponding authors: kylee1@korea.ac.kr (K. Lee), sjkwon@konkuk.ac.kr (S. J. Kwon)

## Material Characterizations

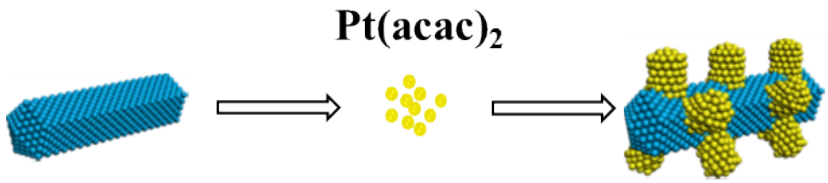
Transmission electron microscopy (TEM) and high-resolution TEM were performed on a TECNAI G2 20 S-Twin operated at 200kV and TECNAI G2 F30 operated at 300 kV. X-ray diffraction (XRD) patterns were collected with a Rigaku UltimaⅢdiffractometer system using a graphite-monochromatized Cu-Kα radiation at 40kV and 40mA.

## Experimental Section

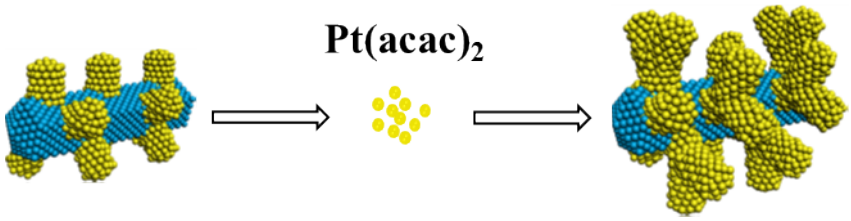
**Preparation of $Pt_3Ni$ nanorod (Fig. 1a,b):** A slurry of $Pt(acac)_2$ (0.06 mmol), $Ni(acac)_2$ (0.02 mmol), ethylene glycol (1.86 mmol) and octadecylamine (15 mmol) was prepared in a 15 mL two-neck round bottom flask with a magnetic stirring. After being evacuated for 120 min with stirring at 80 $^oC$, the resulting solution was charged by CO gas and then heated up to 150 $^oC$, and kept at that temperature for 120 min under CO gas. Finally, dark brown precipitates could be obtained by cooling down the solution to room temperature and then by centrifugation with added methanol / toluene (v / v = 15 mL / 15 mL).

**Preparation of Pt nanorod (Fig. S1a,b):** The method is similar to the preparation of $Pt_3Ni$ nanorod, with the amount of $Pt(acac)_2$ (0.06 mmol) and no $Ni(acac)_2$ used.

**Growth Pt on the $Pt_3Ni$ nanorod to give a worm-like structure (Fig. 1c,d):** $Pt_3Ni$ nanorod (~ 2 mg) were dispersed in a mixture of $Pt(acac)_2$ (0.05mmol), ethylene glycol (1.86 mmol) and octadecylamine (15 mmol) in a two-neck round bottom flask (15 mL) with a magnetic stirring at 80 °C. After being evacuated for 10 min with stirring at 80 °C, the resulting solution was kept at the same temperature for 20 h under Ar gas condition. Finally, dark brown precipitates could be obtained by cooling down the solution to room temperature and then by centrifugation with added methanol / toluene (v / v = 15 / 15 mL).




**Further branch growth from a worm-like $Pt_3Ni$@Pt structure to give a dendritic structure (Fig. 1e):** The method is similar to the growth Pt on the $Pt_3Ni$ nanorod, except for usage of ~2 mg worm-like $Pt_3Ni$@Pt as the seed.




**Growth Pt on the Pt nanorod to give a worm-like structure (Fig. S1c,d):** The method is similar to the growth Pt on the surface of $Pt_3Ni$ nanorod, except for usage of ~2 mg Pt nanorod as the seed.

**Further branch growth from a worm-like Pt@Pt structure to give a dendritic structure (Fig. S1e):** The method is similar to the preparation of growth Pt on the $Pt_3Ni$ nanorod, except for usage of ~2 mg worm-like $Pt_3Ni$@Pt as the seed.

**Fig. S1** TEM and HRTEM images of (a, b) thin Pt nanorods and (c, d) worm-like Pt@Pt nanostructures. (e) TEM image of dendritic Pt@Pt. (f) magnified image of selected area in (d) (inset: FFT image along the [110] zone axis).

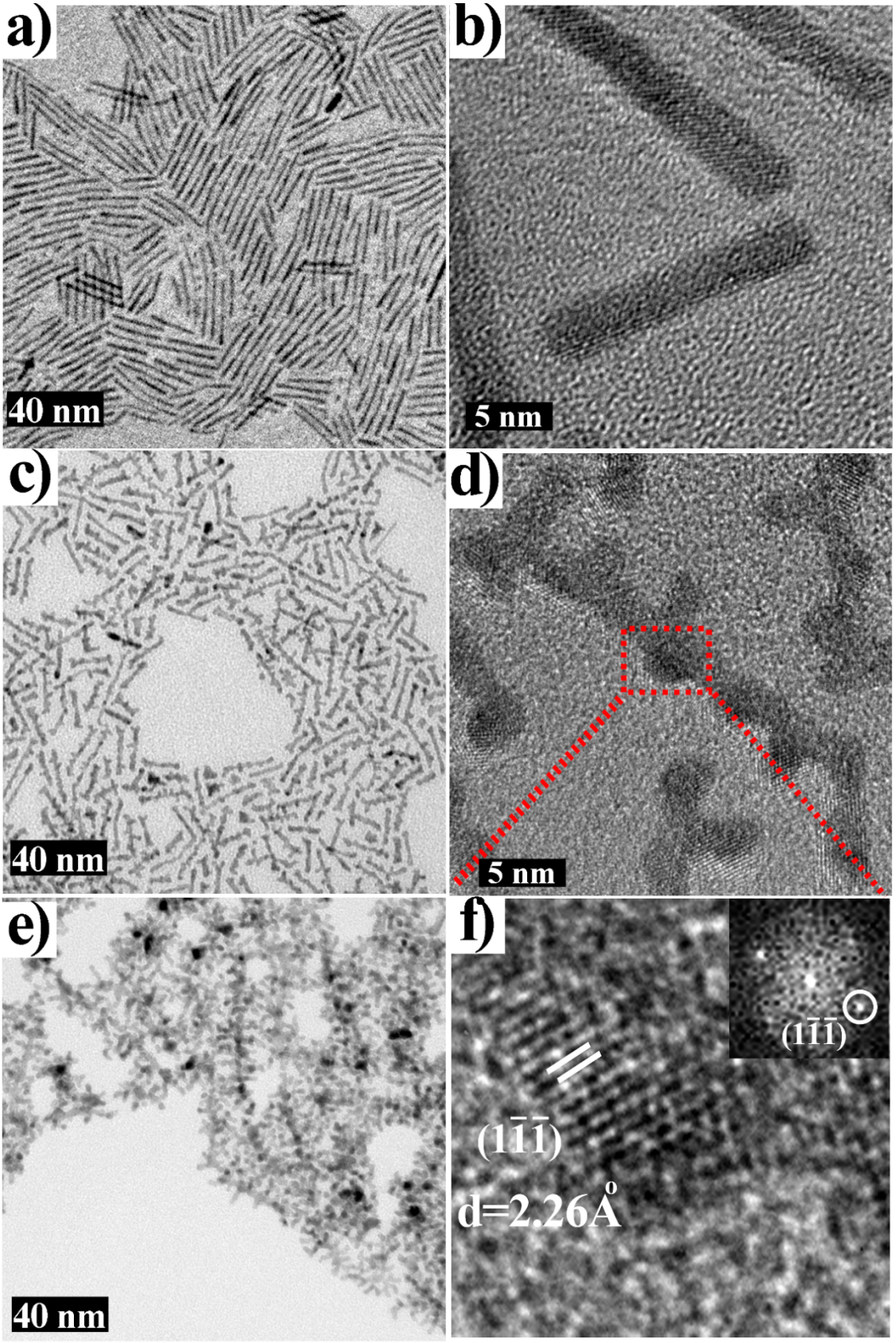
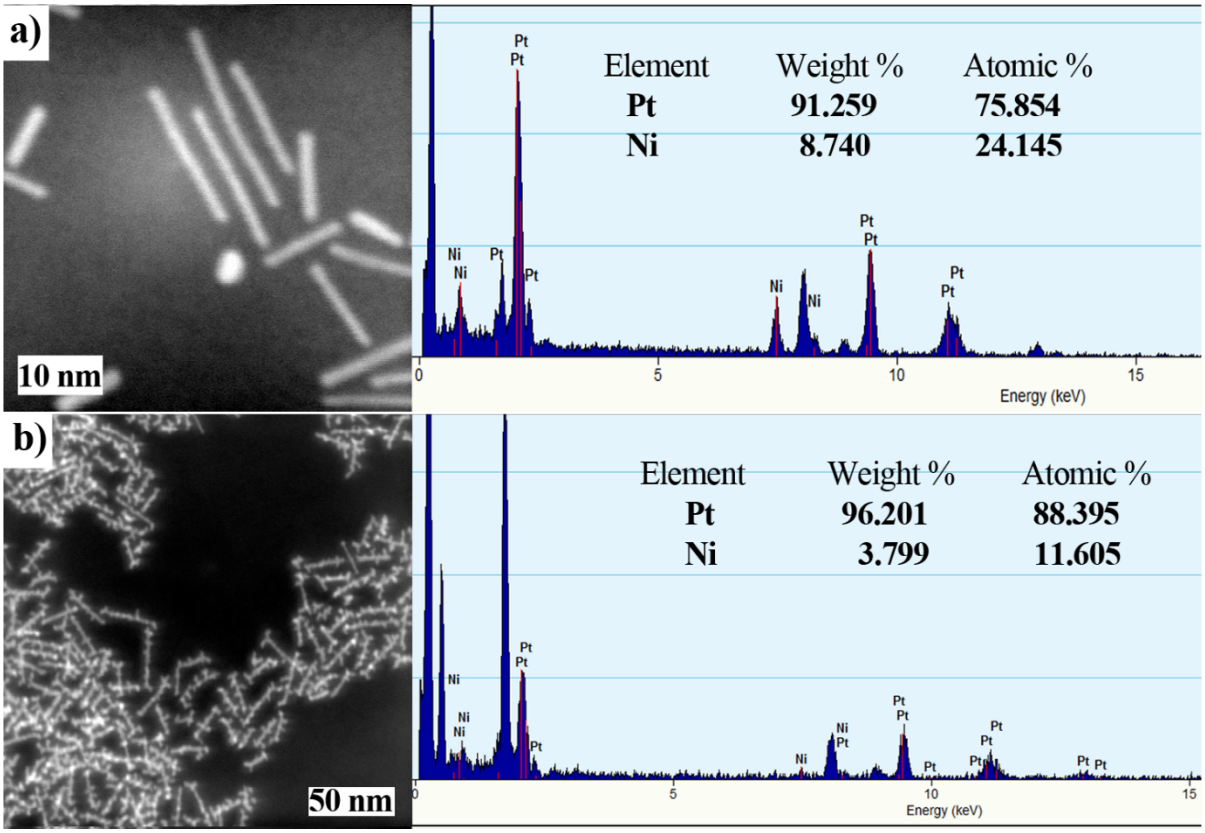


**Fig. S2** Energy dispersive X-ray spectrum of a) thin $Pt_3Ni$ nanorod and b) worm-like $Pt_3Ni$@Pt nanostructucture. We have tried the EDAX analysis for the hierarchical $Pt_3Ni$@Pt nanostructure. However, in this case, the Ni signal was not distinguishable from the background noise and could not be quantified with sufficient accuracy.




**Electrochemical experiment and instruments**

Disk type glassy carbon electrode (GCE) (dia. 3 mm, CH Instruments, Austin, TX) was used as support for Pt nanostructures. GCE was polished with 1.0 and 0.3 μm alumina powder on a polishing cloth (BASi, West Lafayette, IN) followed by sonication in water for 5 min. The electrodes were then rinsed with water and dried. Next, 20 $\mu$L of Nafion solution (1/100 diluted from 5 wt. % stock solution, Aldrich) was dropped on the cleaned GCE and it is dried for 30 min. Each 1 mg of Pt nanostructures were dispersed in 1 mL of methanol by 10 min of sonication. Then 10 $\mu$L of the nanostructure dispersed solution was dropped on the Nafion covered GCE and dried for at least 1 h. The electrochemical experiment was performed using a CHI model 660d potentiostat (CH Instruments, Austin, TX). The general three-electrode electrochemical cell consisted of a modified GC working electrode, an Au wire counter electrode, and a $Hg/Hg_2SO_4$, $K_2SO_4$(sat'd) reference electrode (0.64 V vs. NHE) was used. All the potential in this paper were reported after converting vs. NHE. The electrolyte solution for Oxygen Reduction Reaction (ORR) was 0.5 M $H_2SO_4$ (saturated $O_2$) and for Methanol Oxidation Reaction (MOR) was 10 mL 0.5 M

$H_2SO_4$ and 0.5 M methanol. The ECSA was calculated by measurement the hydrogen desorption peak in Ar-saturated 0.5 M $H_2SO_4$.

**Fig. S3** Chronoamperometry curves at 0.84 V (vs NHE) of nanostructures modified GCE in 0.5 M MeOH + 0.5 M $H_2SO_4$ electrolyte solution.

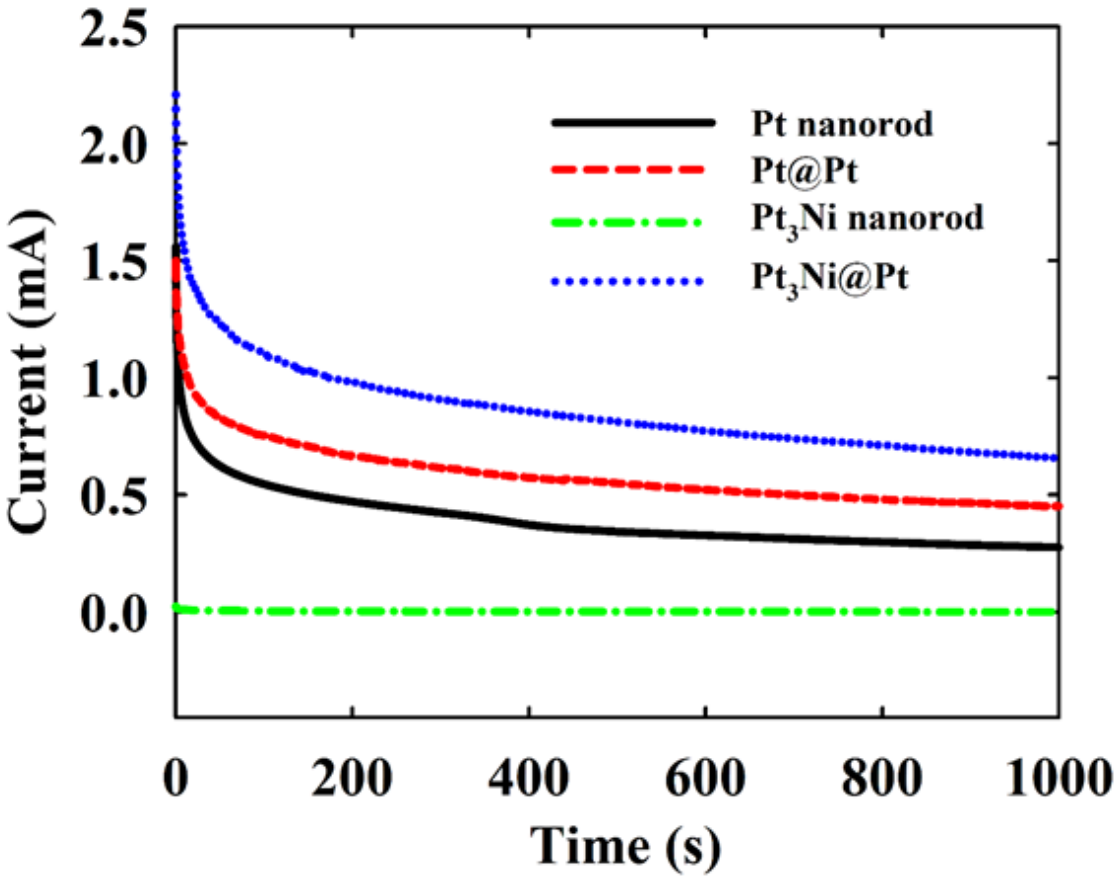


**Fig. S4** TEM images of hierarchical $Pt_3Ni$@Pt a) after surfactant removal and b) after electrocatalytic measurements.

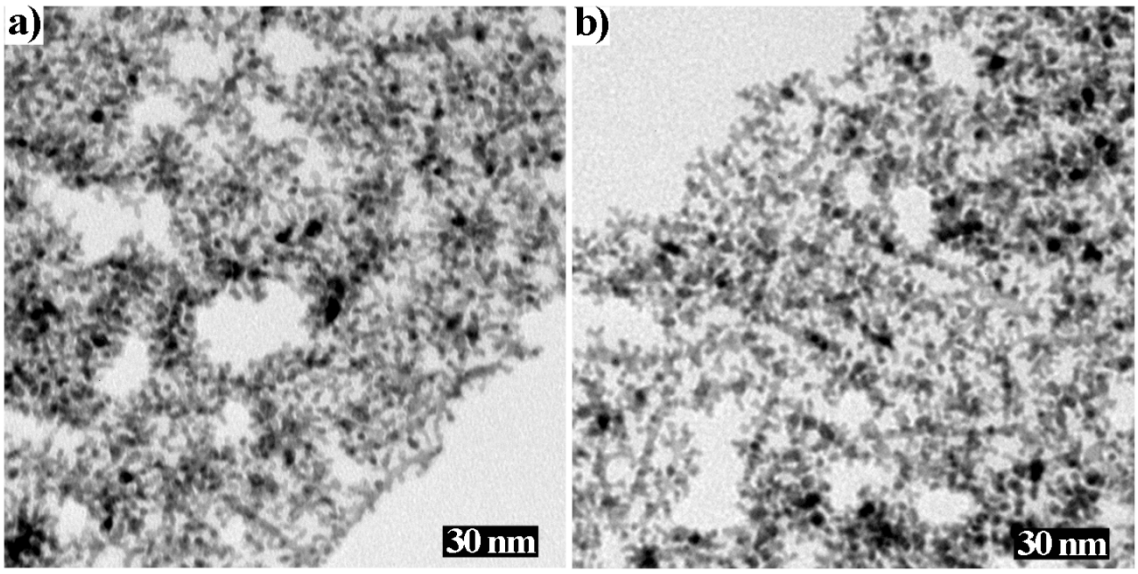



**Fig. S5** X-ray diffraction patterns: a) thin Pt nanorod (JCPDS card no. 04-0802); b) thin $Pt_3Ni$ nanorod; c) dendritic $Pt_3Ni$@Pt (Fig. 1c).