

## Electronic Supplementary Information

### **One-pot synthesis of ultralong coaxial Au@Pt nanocables with numerous highly catalytically active perpendicular twinning boundaries and Au@Pt core-shell bead structures**

*Jisun Yoon<sup>†</sup>, Hionsuck Baik<sup>\*‡</sup>, Sangmin Lee<sup>+</sup>, Seong Jung Kwon<sup>\*+</sup>, and Kwangyeol Lee<sup>\*†</sup>*

<sup>†</sup>Department of Chemistry and Research Institute for Natural Sciences, Korea University, Seoul 136-701 (Korea)

<sup>‡</sup>Korea Basic Science Institute (KBSI), Seoul 136-713 (Korea)

<sup>+</sup>Department of Chemistry, Konkuk University, Seoul 143-701 (Korea)

\*Corresponding authors : kylee1@korea.ac.kr (K. Lee), sjkwon@konkuk.ac.kr (S. J. Kwon), baikhs@kbsi.re.kr (H. Baik)

## Material Characterizations

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were performed on a TECNAI G2 20 S-Twin operated at 200kV and TECNAI G2 F30 operated at 300 kV. Elemental mapping and energy dispersive X-ray spectra (EDX) were obtained with a FEI Titan Cubed 60-300 with Chemi-STEM technology and a JEOL ARM200F Cs STEM. X-ray diffraction (XRD) patterns were collected with a Rigaku Ultima III diffractometer system using a graphite-monochromatized Cu-K $\alpha$  radiation at 40kV and 40mA. The electrochemical experiment was performed using a CHI model 660d potentiostat (CH Instruments, Austin, TX).

## Experimental Section

### *Preparation of Pt-doped Au nanowires*

[1] A slurry of Pt(acac)<sub>2</sub> (0.1 mmol, Aldrich, 97%), HAuCl<sub>4</sub>·xH<sub>2</sub>O (0.1 mmol, Aldrich, 99.999%) and oleylamine 6 mL (Aldrich, 70%) was prepared in a two-neck bottom flask (50 mL) with a magnetic stirring. The flask, placed in the oil bath, was heated to 60 °C and then evacuated for 10 min with magnetic stirring, and finally purged with CO gas. Resulting reaction mixture was heated up to 90 °C at a heating rate of 3 °C/min, and kept at that temperature for 6 h.

**Purification:** The reaction mixture, after being cooled down to room temperature and being added 2 mL toluene, was centrifuged at 2500 rpm for 15 min. The resulting precipitates, after removing the supernatant, were further purified by washing with methanol/toluene (v/v = 1/2 mL) and then by centrifugation at 3500 rpm for 5 min.

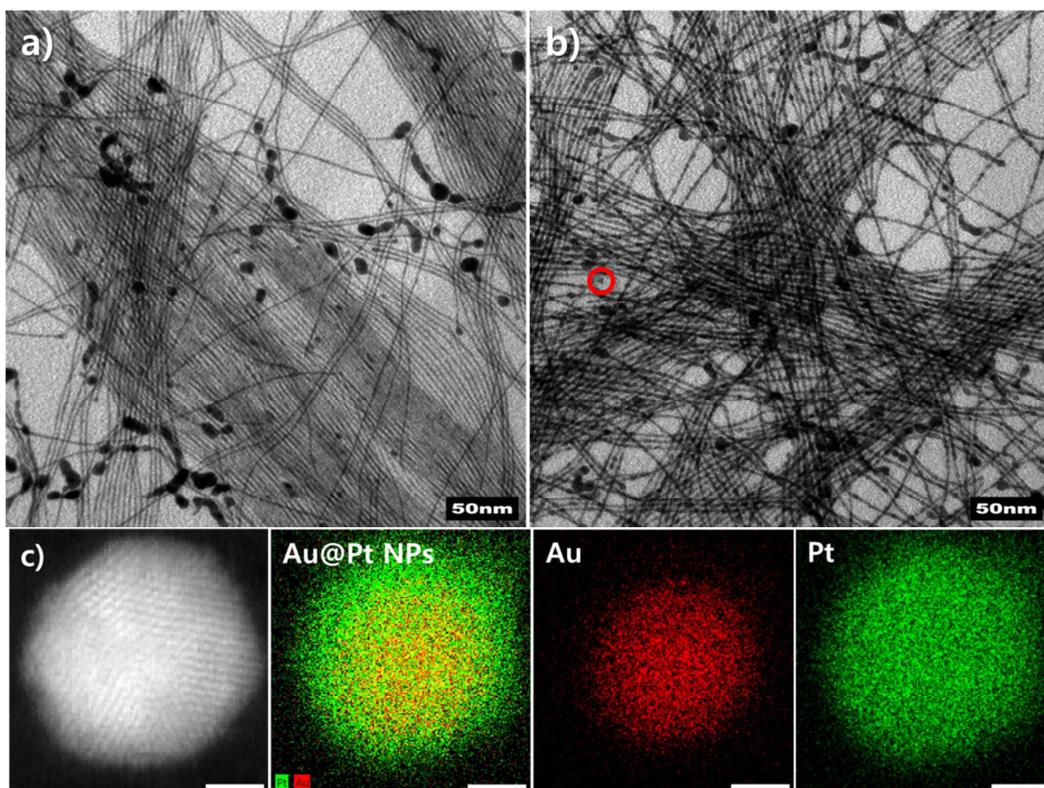
### *Preparation of Au@Pt nanocables*

After step [1] underlined above, reaction mixture was heated up to 210 °C at a heating rate of 8 °C/min and kept at that temperature for 1 min. The reaction mixture, after being cooled down to room temperature and being added 2 mL toluene, was centrifuged at 2500 rpm for 15 min. The resulting precipitates, after removing the supernatant, were further purified by washing with methanol / toluene (v/v = 1/2 mL) and then by centrifugation at 3500 rpm for 5 min.

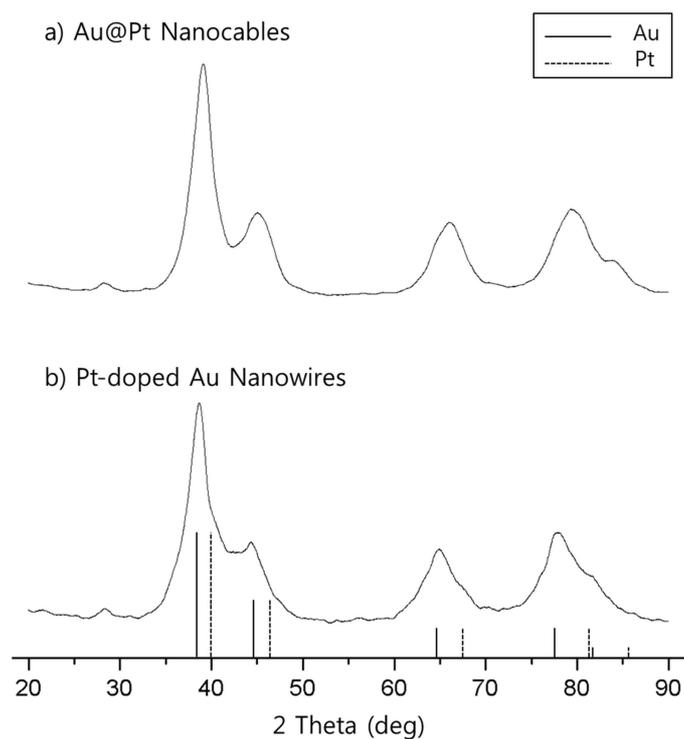
### ***Electrochemical measurements***

Nafion® perfluorinated resin solution (5 wt. % in lower aliphatic alcohols and water) was purchased from Aldrich. Pt nanocubes and nanorods were prepared by following previous work.<sup>1</sup>

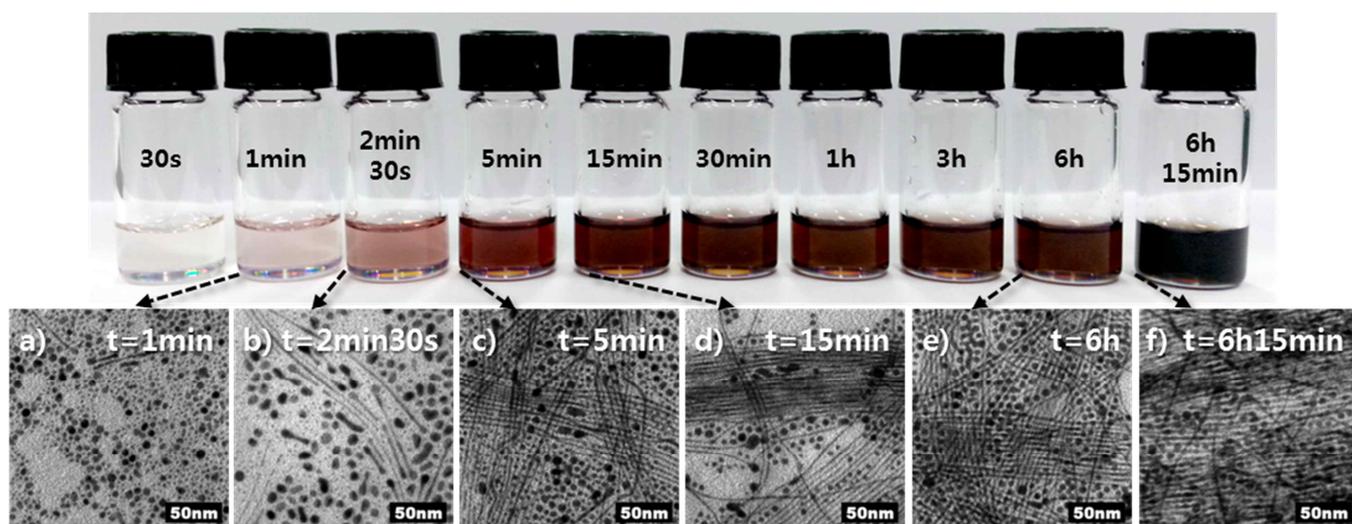
Glassy carbon disk electrodes (GCE) (dia. 3 mm, CH Instruments, Austin, TX) were used as support for Pt NPs. GCE were prepared by polishing with 1.0 and 0.3  $\mu\text{m}$  alumina powder on a polishing cloth (Buehler) followed by sonication in water for 5 min. The electrodes were then rinsed with water and dried. 10  $\mu\text{L}$  of Nafion® solution (1/100 diluted from 5 wt. % stock methanol solution) was dropped on the cleaned GCE and dried for 30 min. The prepared 2 mg Pt NP (rod and cube) were dispersed in 7 mL of methanol by 10 min of sonication. The prepared 2.4 mg Au@Pt NWs were dispersed in 6 mL of isopropanol with 75  $\mu\text{L}$  of nafion by 10 min of sonication. Then 10  $\mu\text{L}$  of each Pt NP stock solution was dropped on the Nafion® coated GCE and dried for at least 1 h. The three-electrode electrochemical cell consisted of a modified GC working electrode, an Au wire counter electrode, and a Hg/Hg<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>(sat'd) reference electrode (0.64 V vs. NHE) was used. All the potential in this paper was reported vs. NHE. Oxygen Reduction Reaction (ORR) was performed in 0.5 M H<sub>2</sub>SO<sub>4</sub> (saturated O<sub>2</sub> or Ar) and Methanol Oxidation Reaction(MOR) was performed in 10 mL 0.5 M H<sub>2</sub>SO<sub>4</sub>.



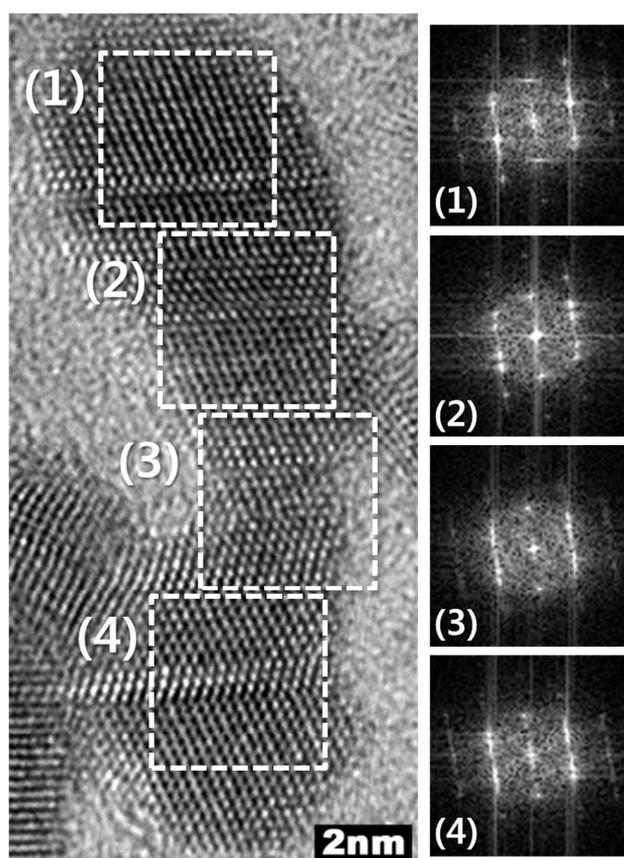
**Fig. S1** TEM images of (a) Pt doped-Au nanowires and (b) Au@Pt nanocables. (c) Elemental mapping of Au@Pt nanoparticle which is the side product in the reaction. A side product nanoparticle is indicated by a red circle in (b). The scale bar is 2 nm.



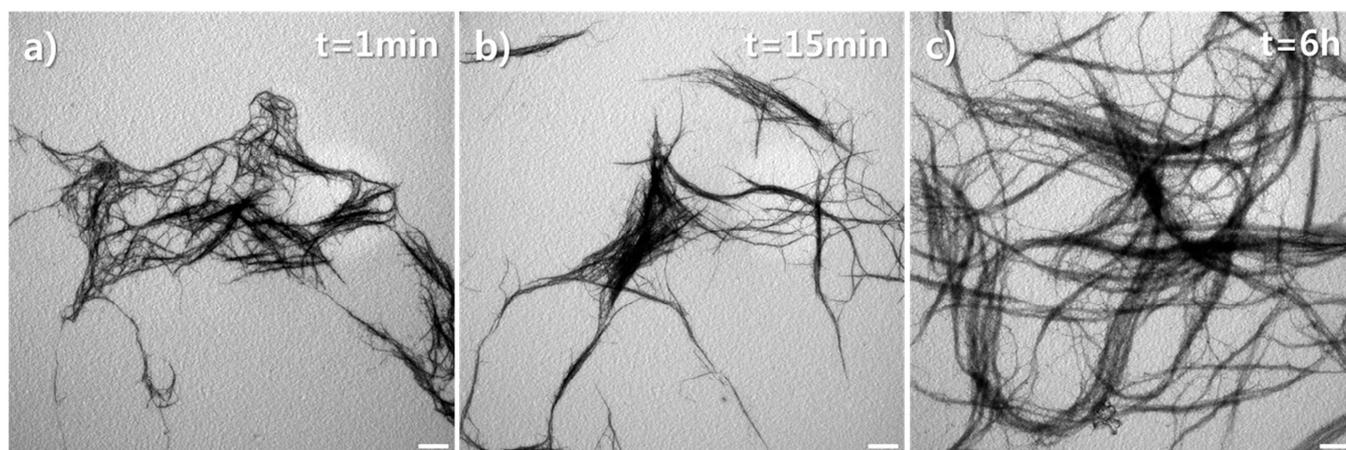
**Fig. S2** X-ray diffraction patterns of a) Au@Pt nanocables and b) Pt-doped Au nanowires. (JCPDS card no. 71-3755(Au), 70-2057 (Pt)).



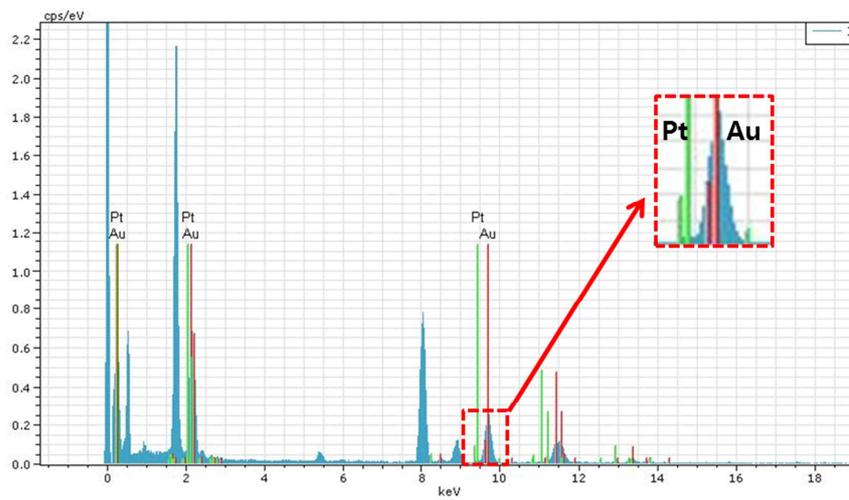
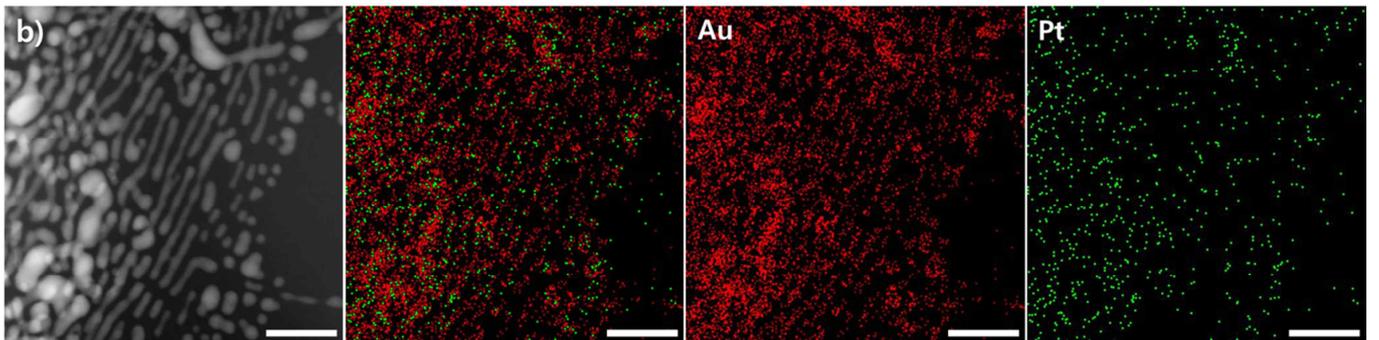
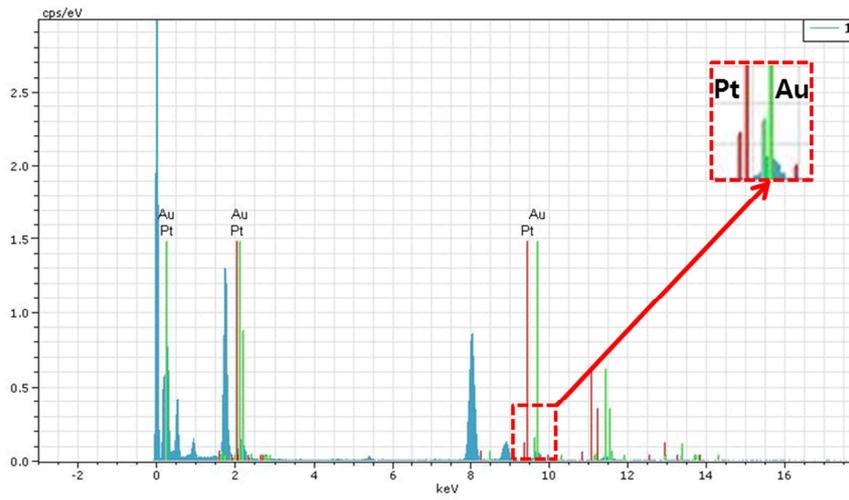
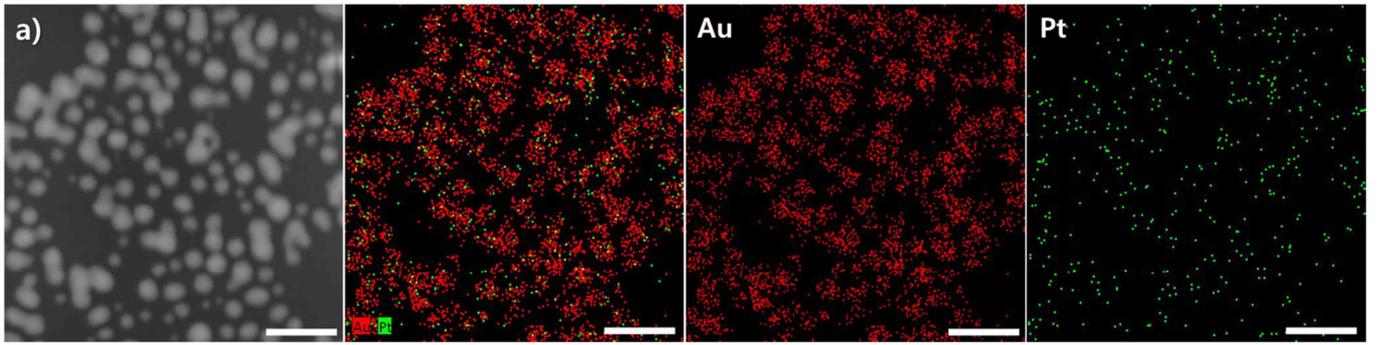
**Fig. S3** The photographs of reaction mixtures at different reaction time as well as corresponding TEM images. (a-e) TEM images obtained at (a) 1 min, (b) 2 min 30 s, (c) 5 min, (d) 15 min and (e) 6 h: reaction at 90 °C (f) TEM image of Au@Pt nanowires and nanoparticles synthesized at 210 °C.

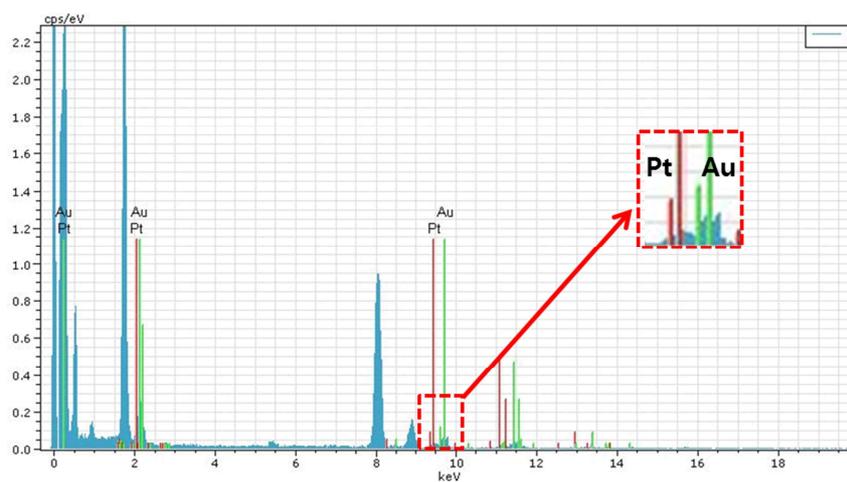
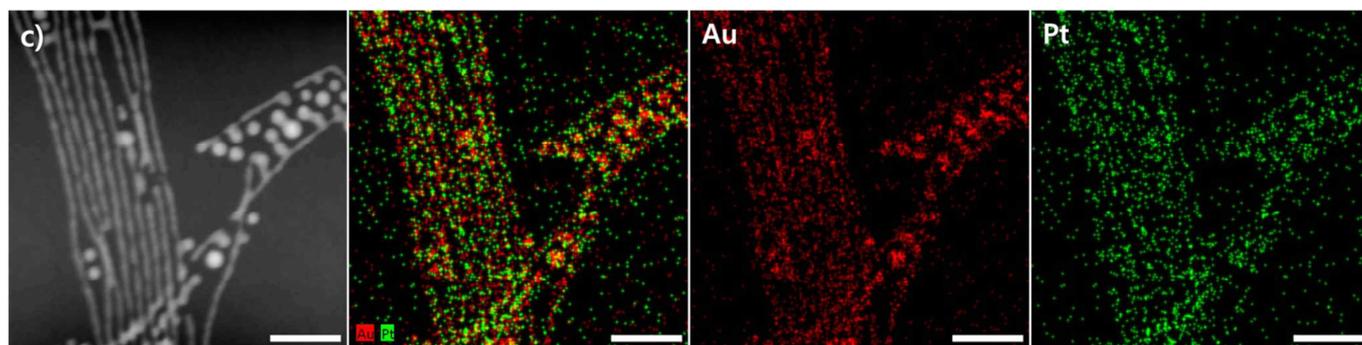


**Fig. S4** HR-TEM image and FFT patterns of the dumbbell shaped Pt-doped Au nanoparticle. The corresponding FFT patterns show the highly twinned nature of the nanostructure.



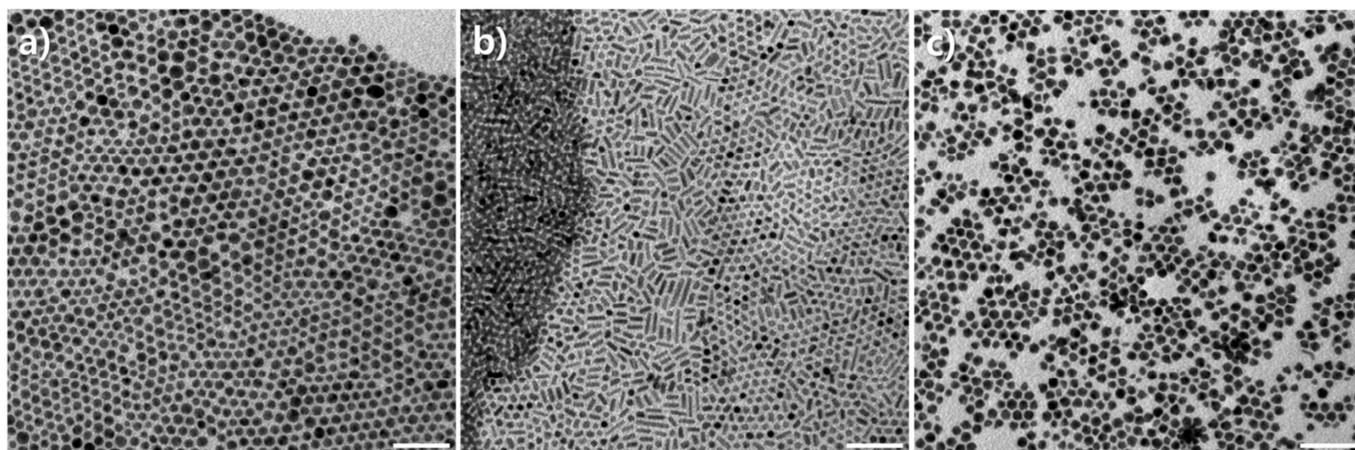
**Fig. S5** TEM images of Pt-doped Au nanowires prepared at different reaction time. Pt-doped Au nanowires with the length of a) 2~3  $\mu\text{m}$ , b) 3~4  $\mu\text{m}$ , and c) 7~10  $\mu\text{m}$ . The scale bar is 1  $\mu\text{m}$ .



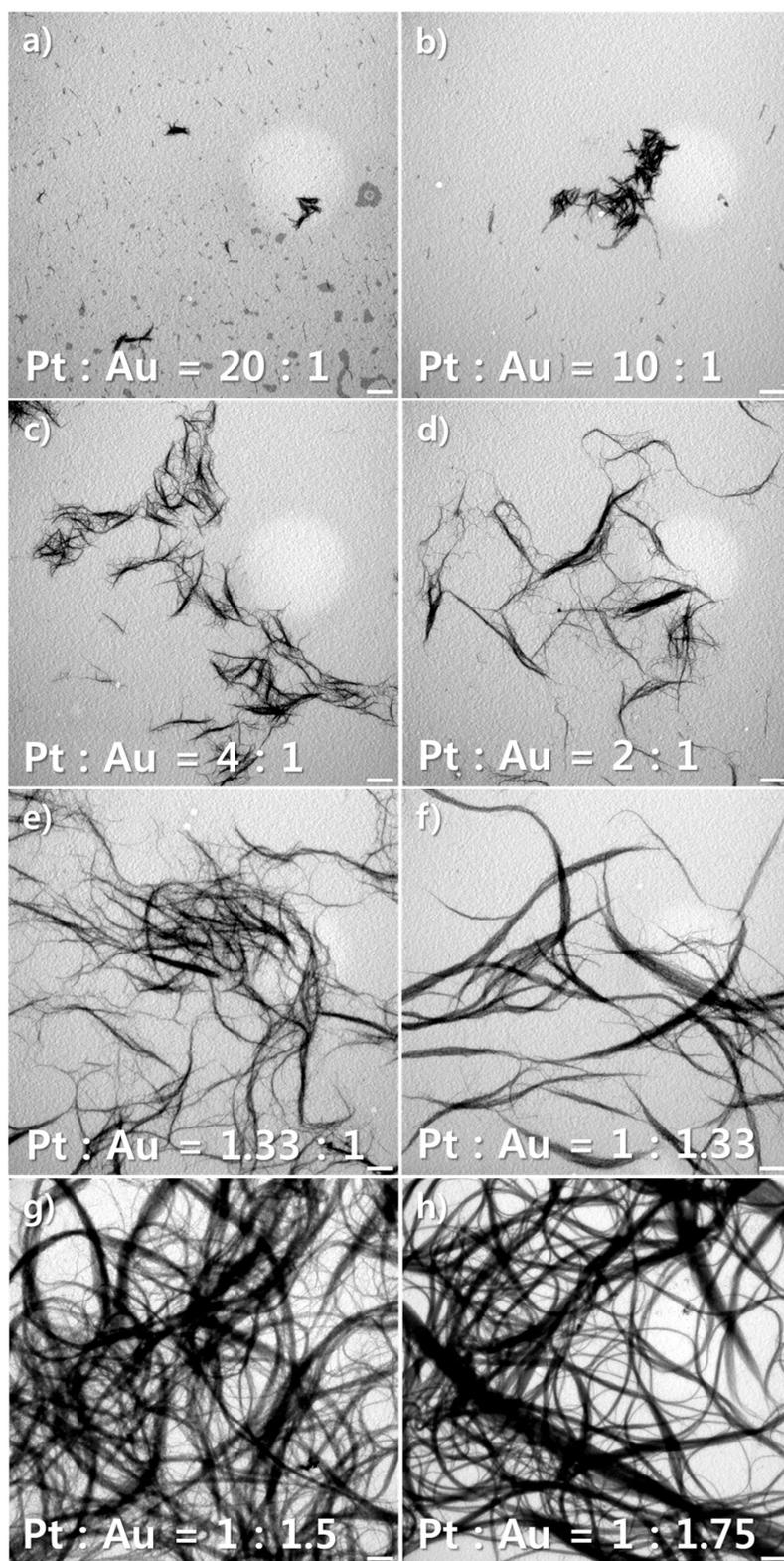


Reaction time at 90 °C	The percent of Pt	The percent of Au
5min	under 2	above 98
15min	2.2	97.8
6h	19.8	80.2

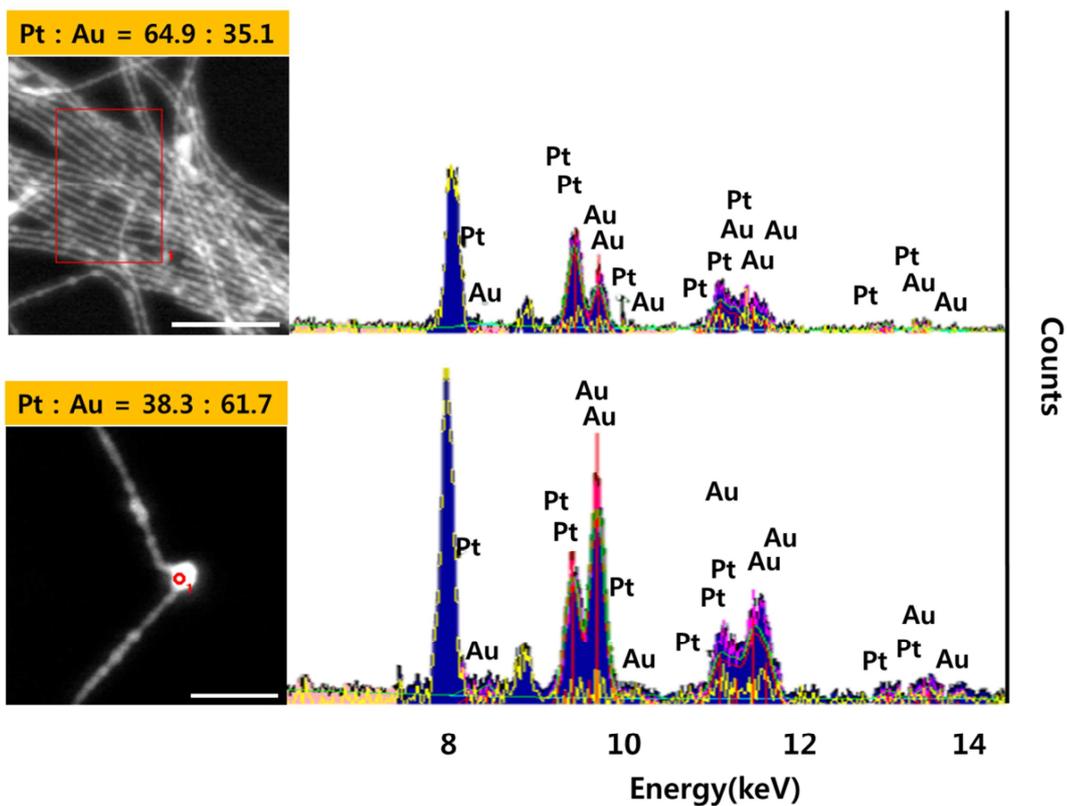
**Fig. S6** Elemental mapping and EDX data of Pt-doped Au nanowires synthesized at 90 °C after different reaction times of a) 5 min b) 15min c) 6h. The relative quantity of Pt in Au nanowires increased as reaction went on (see the table). The final ratio of Pt to Au in Pt-doped Au nanowires after 6 h reaction became 19.8% to 80.2%. The scale bar is 20nm.



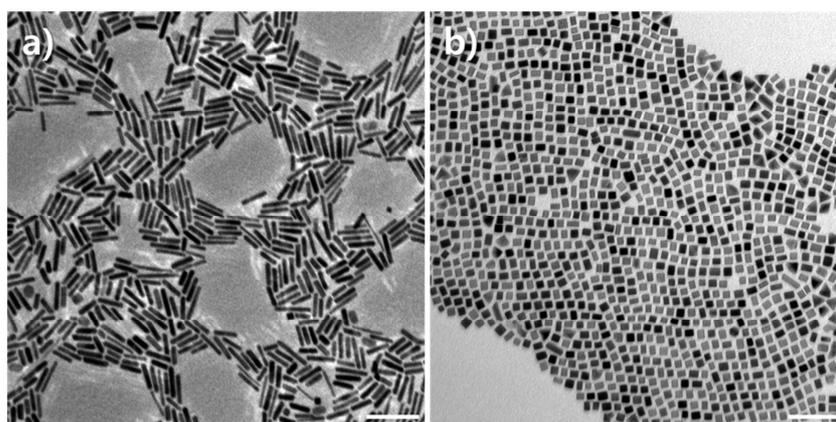
**Fig. S7** TEM images of a) Au nanoparticles synthesized with the same condition of Au@Pt nanocables without Pt(acac)<sub>2</sub> and b) Pt nanoparticles synthesized with the same condition of Au@Pt nanocables without H<sub>2</sub>AuCl<sub>4</sub>·xH<sub>2</sub>O. c) Au@Pt nanoparticles prepared under Ar. The scale bar is 50 nm.



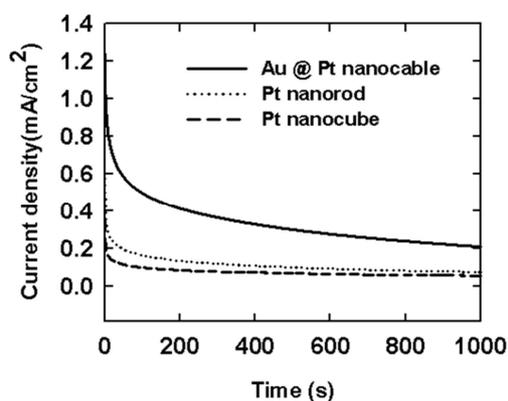
**Fig. S8** TEM images of Au@Pt nanocables synthesized by using the different molar ratio of  $\text{Pt}(\text{acac})_2$  to  $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ . As the amount of  $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$  increases, nanocables are more elongated. Au@Pt nanocables with the length of a, b)  $\sim 1 \mu\text{m}$ , c)  $1\sim 2 \mu\text{m}$ , d)  $2\sim 3 \mu\text{m}$ , e)  $3\sim 5 \mu\text{m}$ , f)  $4 \sim 10 \mu\text{m}$ , and g) above  $10 \mu\text{m}$ . The scale bar is  $1 \mu\text{m}$ .



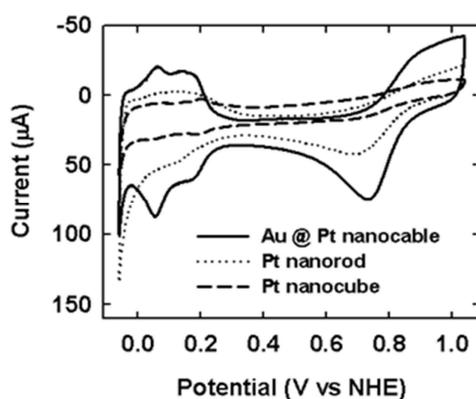
**Fig. S9** EDX data of Au@Pt nanocables. The elemental distributions along nanowire were assessed at various parts of the nanowire. (a) The average ratio of Pt to Au in Au@Pt nanocables was 65% to 35%. (b) Occasionally, large Au nanoparticles at the kinked positions were observed. The scale bars are (a) 50 nm and (b) 20 nm.



**Fig. S10** TEM images of a) Pt nanorods and b) Pt nanocubes.



**Fig. S11** Chronoamperometry curves of Pt nanostructures-modified GCE in 0.5 M MeOH + 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte solution. Scan rate was 50 mV/s.



**Fig. S12** Cyclic voltammograms of Pt nanostructures-modified GCE in O<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte solution. Scan rate was 50 mV/s.

Nanostructure	ECSA (m <sup>2</sup> /g)	Current density (mA/cm <sup>2</sup> )	Mass activity (mA/mg)
Au @ Pt nanocable	76.5	0.133	102
Pt nanorod	13.8	0.244	33.5
Pt nocube	13.9	0.119	16.5

**Table. S1** Electrocatalytic properties of Pt nanostructures for ORR. We used same samples for the both ORR and MOR measurement in case of nanorod and nanocube. However, different samples were used for the ORR and MOR in case of nanocable. That caused a small difference in ECSA in table 1 and table S1. Also, the ORR currents of nanostructures were quite low compare with the MOR currents of nanostructures. The current density in table S1 was obtained as the peak current divided by its ECSA. The experiment was done in stationary disk electrode not the rotating disk electrode (RDE). This might have caused the low current values.

## Reference

1. J. Yoon, N. T. Khi, H. Kim, B. Kim, H. Baik, S. Back, S. Lee, S. W. Lee, S. J. Kwon and K. Lee, *Chem. Commun.*, 2013, **49**, 573.