

Supporting Information

Multi-Layered Pt/Ni Nanotube Arrays with Enhanced Catalytic Performance for Methanol Electrooxidation

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Experimental Section

Fabrication of ZnO nanorod arrays (NRAs) template. All chemical reagents were analytical grade. Electrodeposition was carried out in a simple two-electrode electrolytic cell via galvanostatic electrodeposition, and the graphite electrode was used as a counter electrode (spectral grade, 1.8 cm²). The Ti plate (99.99%, 1.0 cm²) was used as a working electrode, and it was prepared complying the following steps before each experiment: firstly polished by SiC abrasive paper from 300 to 800 grits, then dipped in HCl solution (5%) for 10 min and rinsed with acetone in ultrasonic bath for 5 min, and finally washed by distilled water. The electrodeposition of ZnO NRAs was carried out on Ti substrate in 0.01 mol/L Zn(NO₃)₂ + 0.05 mol/L NH₄Cl solution at 0.4 mA/cm² at 70 °C for 1.5 h. SEM image of ZnO NRAs is shown in Figure S1.

Synthesize of Pt/Ni MLNTAs. The various Pt/Ni multi-layered nanotubes arrays (MLNTAs), such

as Ni@Pt NTAs, Ni@Pt@Ni@Pt NTAs, Pt@Ni@Pt NTAs, and Pt@Ni@Pt@Ni@Pt NTAs were fabricated by using ZnO NRAs as templates and layer-by-layer electrodeposition. Here Ni@Pt NTAs were used as an example to illustrate the fabrication of Pt/Ni MLNTAs. Electrodeposition of Ni layer was firstly carried out in solution of 0.01 M Ni(Ac)₂ + 0.05 M H₃BO₃ + 0.05 M NH₄Cl for 20 min at 0.25 mA/cm², and accordingly ZnO@Ni NRAs were fabricated. Then the electrodeposition of Pt layer was carried out on the surfaces of ZnO@Ni NRAs in solution of 20 mM H₂PtCl₆ + 0.5 M NaCl + 2.5 mM sodium citrate for 20 min at 0.25 mA/cm² and accordingly ZnO@Ni@Pt NRAs were fabricated. Finally, ZnO templates were removed by immersing the samples into NH₃·H₂O solution (10%) for 3 h and the Ni@Pt NTAs were successfully fabricated. Other Pt/Ni MLNTAs, such as Ni@Pt@Ni@Pt NTAs, Pt@Ni@Pt NTAs, and Pt@Ni@Pt@Ni@Pt NTAs were fabricated by the similar method. The details of the fabrication procedures of various Pt/Ni MLNTAs please see Scheme S1 and S2 in supporting information. For the comparative study, Pt NTAs were also synthesized by the similar route and their SEM image is shown in Figure S3 (here the electrodeposition of Pt layers on ZnO NRAs is 1h because of the lack of Ni layer).

Structural characterization: The morphologies of samples were characterized by field emission scanning electron microscopy (FE-SEM, JSM-6330F) and transmission electron microscopy (TEM, JEM-2010HR). Chemical-state analysis was determined by X-Ray photoelectron spectroscopy (XPS) using an ESCAKAB 250 X-Ray photoelectron spectrometer, all peaks corrected by C 1s line at 284.6eV as standard, and curve fitting and background subtraction were accomplished. Chemical component analysis was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) using TJA IRIS(HR) spectrometer.

Electrochemical characterization: Electrochemical properties of the prepared electrocatalysts were

studied in a standard three-electrode electrolytic cell. The Pt NTAs, Ni@Pt NTAs, Pt@Ni@Pt NTAs, Ni@Pt@Ni @Pt NTAs and Pt@Ni@Pt@Ni@Pt NTAs grown on Ti substrates served as the working electrodes, respectively. A Pt foil served as the counter electrode. A saturated calomel electrode (SCE) was used as the reference electrode. All potentials were the values *vs* SCE. Cyclic voltammetry (CV) and chronoamperometry were measured by using a CHI660D electrochemical workstation (CH instruments, Inc.). CVs were recorded between -0.20 and 1.00 V *vs* SCE at 50 mV/s. Chronoamperometry curves for methanol electrooxidation were recorded at 0.65 V. For CV and chronoamperometry measurements of methanol electrooxidation reactions, an aqueous solution of 0.5 M H₂SO₄+0.5 M CH₃OH was utilized. All of the electrolyte solutions were purged with high purity N₂ for 10 min, and all the electrochemical measurements were carried out at room temperature.

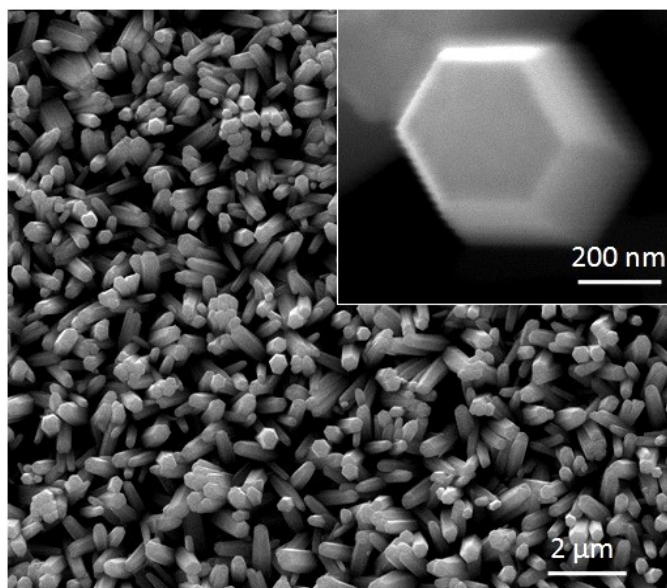
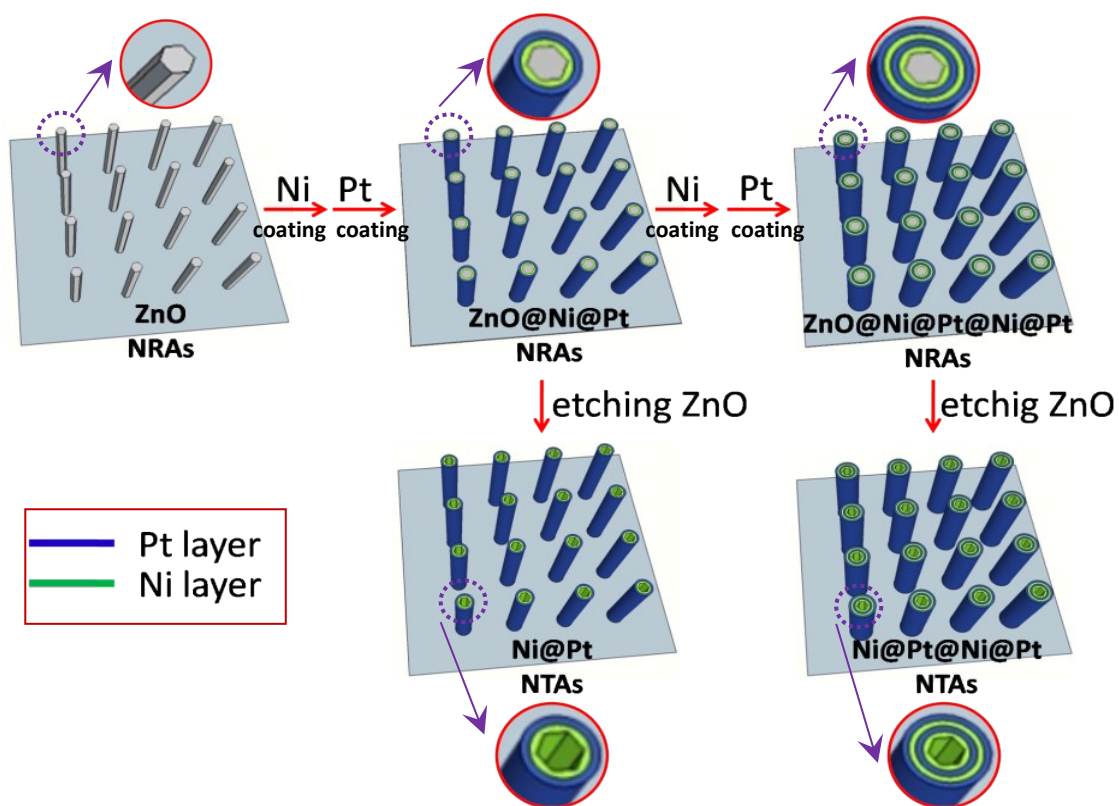
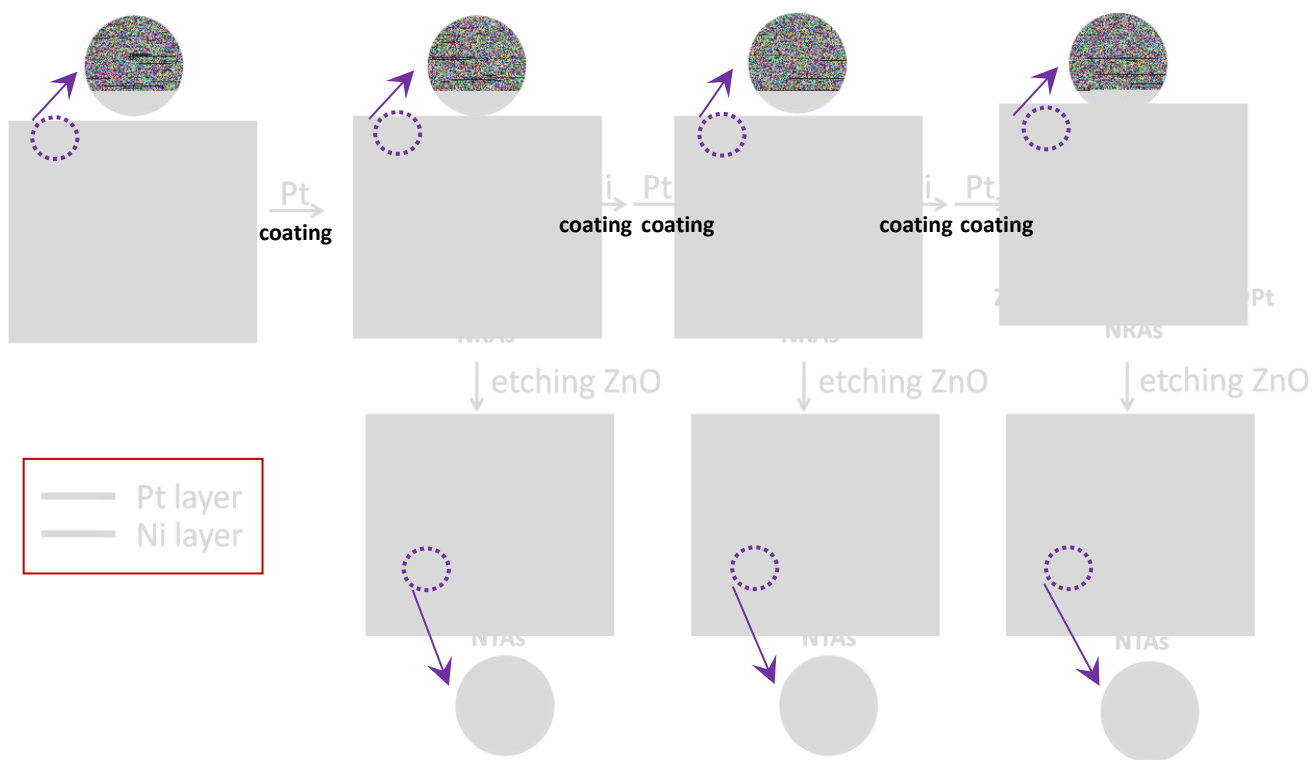


Figure S1. SEM image of ZnO NRAs.



Scheme S1. Schematic illustration for template-assisted fabrication of Ni@Pt NTAs and Ni@Pt@Ni@Pt NTAs by layer-by-layer electrodeposition method.



Scheme S2. Schematic illustration for template-assisted fabrication of Pt NTAs, Pt@Ni@Pt NTAs, and Pt@Ni@Pt@Ni@Pt NTAs by layer-by-layer electrodeposition method.

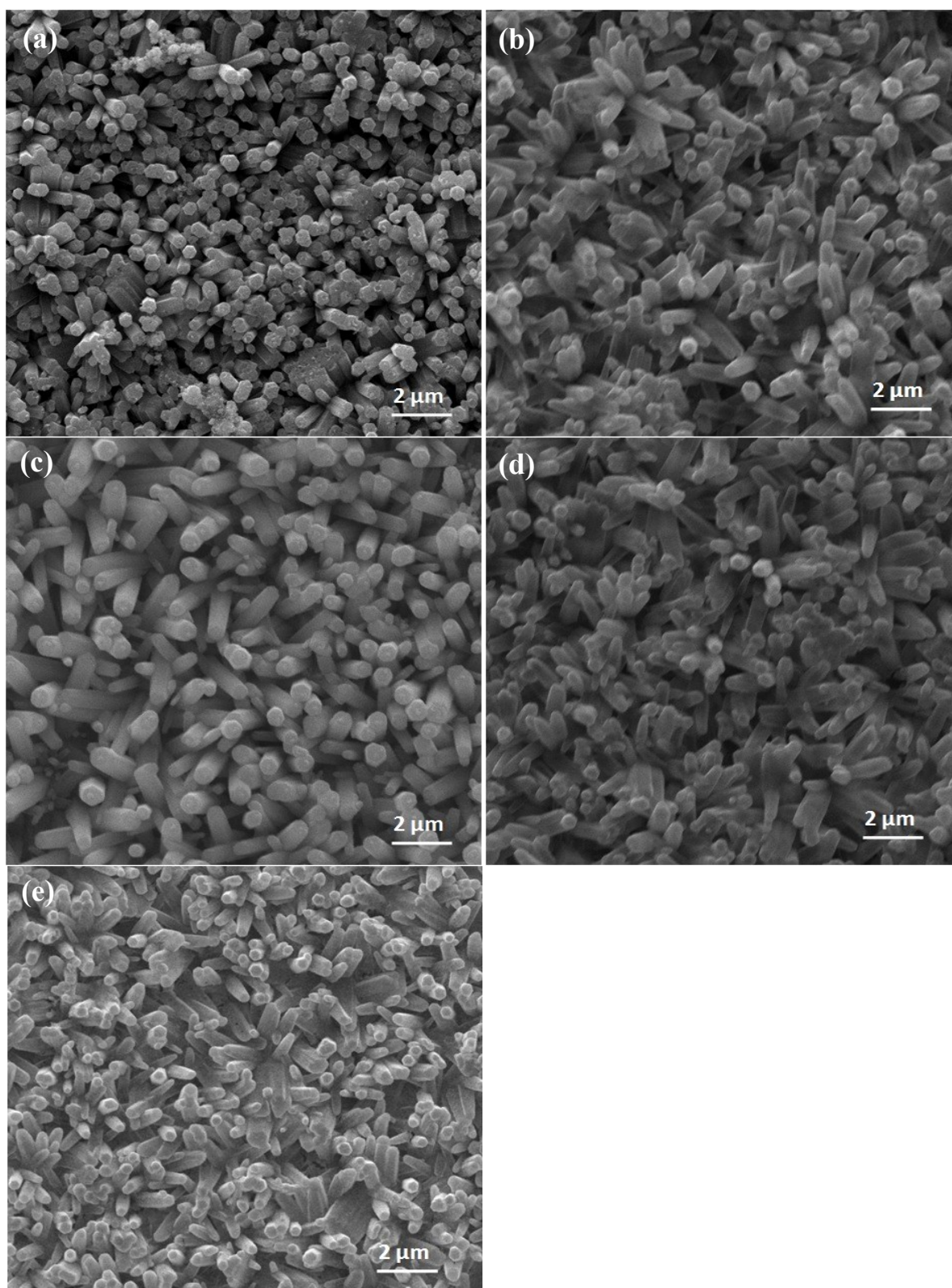


Figure S2. SEM images of (a) ZnO@Pt NRAs; (b) ZnO@Ni@Pt NRAs; (c) ZnO@Pt@Ni@Pt NRAs; (d) ZnO@Ni@Pt@Ni@Pt NRAs; and (e) ZnO@Pt@Ni@Pt@Ni@Pt NRAs.

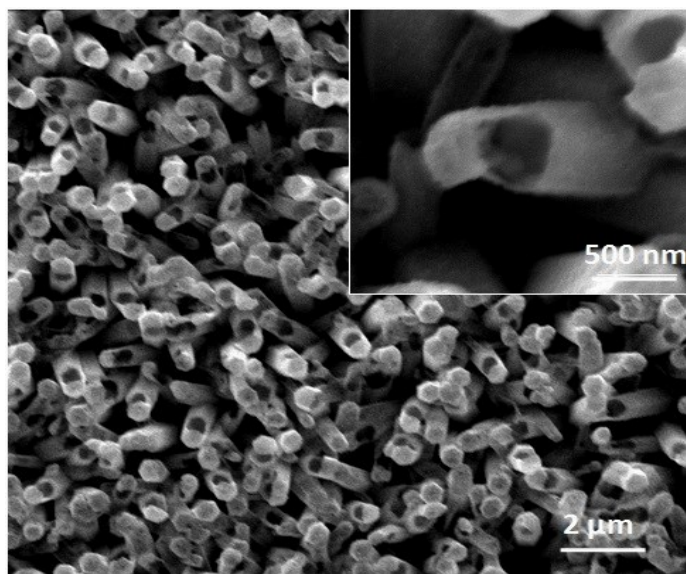


Figure S3. SEM image of Pt NTAs.

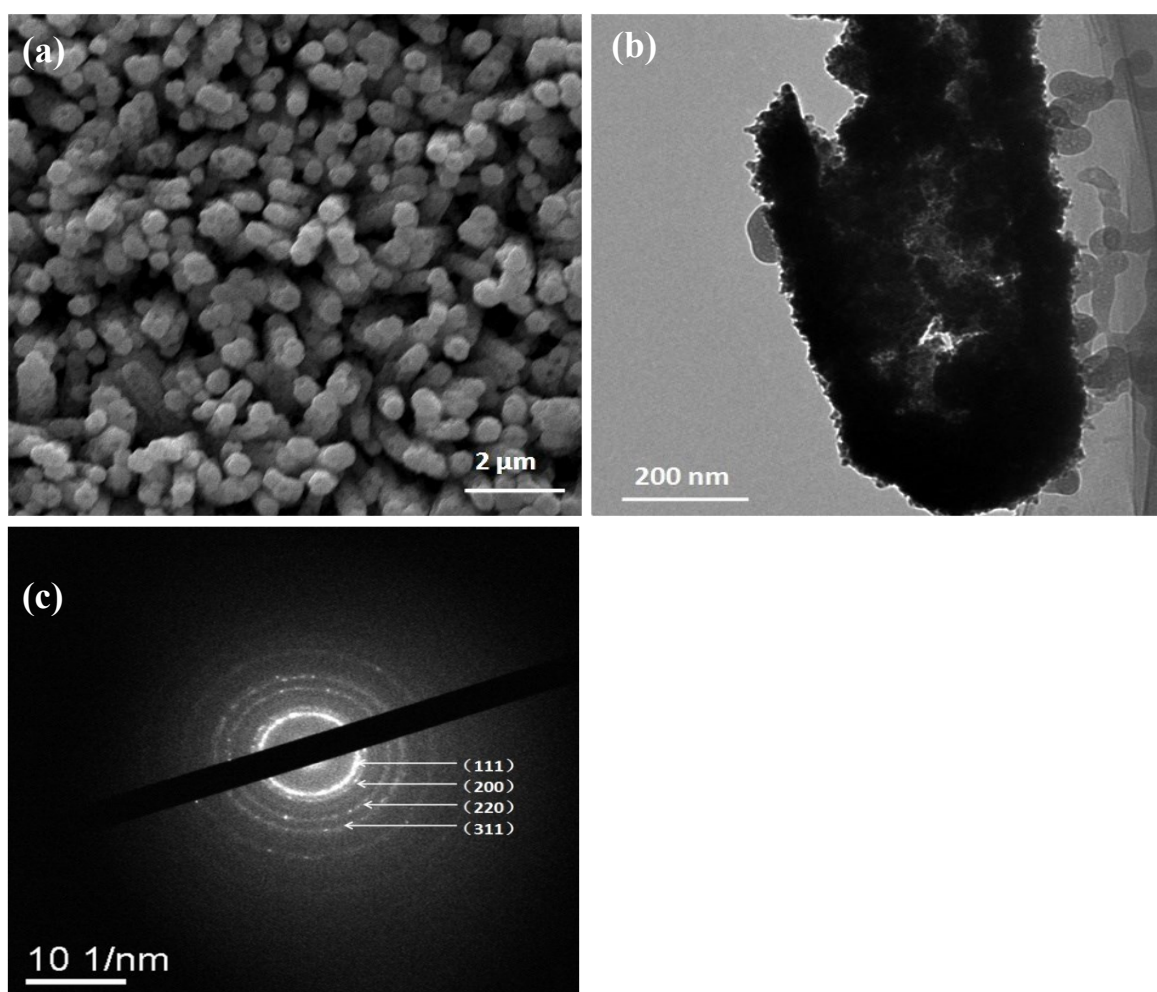


Figure S4. (a) SEM image, (b) TEM image and (c) SAED pattern of Ni nanotubes.

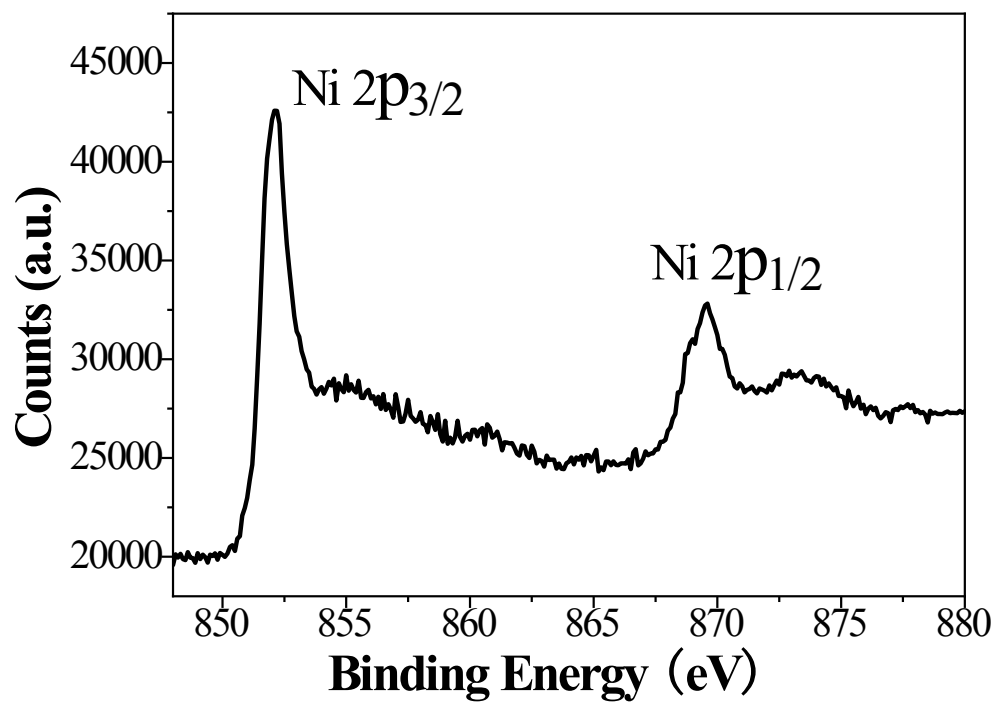


Figure S5. XPS spectra of Ni@Pt@Ni@Pt NTAs in Ni 2p region.

Table S1. Activity comparisons of Ni@Pt@Ni@Pt NTAs with other Pt-based electrocatalysts.

Catalyst	Mass activity mA/mg _{pt}	Testing condotions	Ref.
Ni@Pt@Ni@Pt	362.7	0.5 M H₂SO₄ + 0.5 M CH₃OH 50mV/s	This work
Mesoporous Pt/Pd	~280	0.5 M H ₂ SO ₄ + 0.5 M CH ₃ OH 50mV/s	J. Am. Chem. Soc. 2012 , 134, 10819
Mesoporous Pt/Pd/Pt	~320		
Pt-on-Pd	280	0.5 M H ₂ SO ₄ + 0.5 M CH ₃ OH 50mV/s	J. Am. Chem. Soc. 2011 , 133, 9674
Pt₄₉Te₅₁	249.8	0.5 M H ₂ SO ₄ + 1 M CH ₃ OH 20mV/s	Angew. Cheme. 2013 , 125, 7620
Pt/[BMIM]BF₄/CNT	155	0.5 M H ₂ SO ₄ + 1 M CH ₃ OH 20mV/s	Adv. Funct. Mater. 2010 , 20, 3747
Pt-SiO₂	270	1 M H ₂ SO ₄ + 0.5 M CH ₃ OH 100mV/s	ACS Appl. Mater. Interfaces 2015 , 7, 6590
PtSn/C	250	0.1 M NaOH + 0.5 M CH ₃ OH 20mV/s	ACS Appl. Mater. Interfaces 2015 , 7, 15061
Pt₂₀/C	220	0.5 M H ₂ SO ₄ + 0.5 M CH ₃ OH	J. Mater. Chem. A. 2015 , 3, 18010
Pt₄₀/C	336	50mV/s	
Pt/RGO_{Na}-BH₃	~260	0.5 M H ₂ SO ₄ + 0.5 M CH ₃ OH 50mV/s	Chem. Commun. 2015 , 51, 2418
Pt-sphere	~220	0.5 M H ₂ SO ₄ + 1 M CH ₃ OH 50mV/s	J. Mater. Chem. A 2014 , 2, 13738
Pt/thermal exfoliated graphene	~300	0.5 M H ₂ SO ₄ + 2 M CH ₃ OH 50mV/s	Carbon 2011 , 49, 904
Pt/N-doped graphene	135	0.5 M H ₂ SO ₄ + 0.5 M CH ₃ OH 20mV/s	Chem. Mater. 2009 , 22, 832
PtIr/CNT	311	0.5 M H ₂ SO ₄ + 0.5 M CH ₃ OH 50mV/s	J. Mater. Chem. 2012 , 22, 19658
PdPt/graphene	198	0.1 M HClO ₄ + 1 M CH ₃ OH 50mV/s	J. Phys. Chem. C 2013 , 117, 2926
Pt/MC/graphene	81.6	0.5 M H ₂ SO ₄ + 0.5 M CH ₃ OH 50mV/s	Electrochim. Acta. 2013 , 90, 283
Pt/N-doped CNT	103	0.5 M H ₂ SO ₄ + 1 M CH ₃ OH 20mV/s	J. Mater. Chem. 2012 , 22, 13578
Pt/Sn-modified CNT	91	0.5 M H ₂ SO ₄ + 1 M CH ₃ OH 50mV/s	Chem. –Eur. J. 2010 , 16, 829
Pt/CeO₂ graphene	366	0.5 M H ₂ SO ₄ + 1 M CH ₃ OH 100mV/s	Chem. Commun. 2012 , 48, 2885
Pt-Co NWs	~260	0.5 M H ₂ SO ₄ + 1 M CH ₃ OH 50mV/s	Energy. Environ. Sci. 2011 , 4,

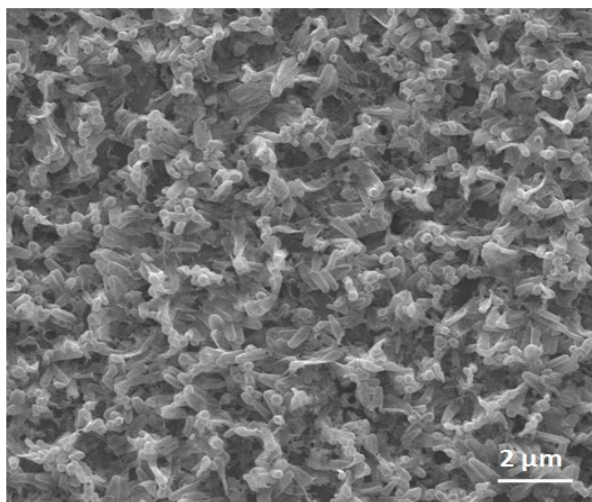


Figure S6. SEM image of Ni@Pt@Ni@Pt NTAs after the electrocatalytic process.

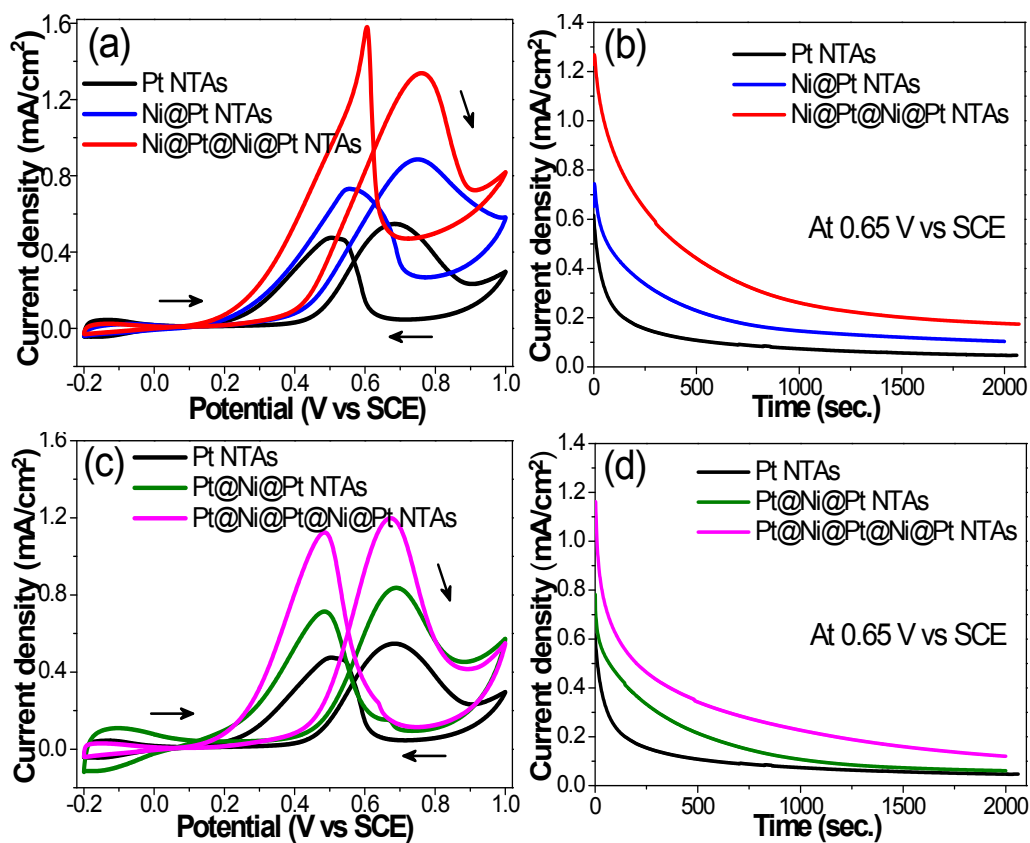


Figure S7. (a) CVs and (b) chronoamperometry curves of Pt NTAs, Ni@Pt NTAs and Ni@Pt@Ni@Pt NTAs in solution of 0.5 M H₂SO₄+0.5 M CH₃OH at 50 mV/s; (c) CVs and (d) chronoamperometry curves of Pt NTAs, Pt@Ni@Pt NTAs and Pt@Ni@Pt@Ni@Pt NTAs in solution of 0.5 M H₂SO₄+0.5 M CH₃OH at 50 mV/s (the current densities all are normalized to ECSA).

Table S2. ECSA and specific activity comparisons of Pt NTAs, Ni@Pt NTAs, Ni@Pt@Ni@Pt NTAs, Pt@Ni@Pt NTAs, and Pt@Ni@Pt@Ni@Pt NTAs (Data comes from Figure 3 in paper and Figure S7 in supporting information).

Sample	Pt loading (mg)	Specific activity (mA/mg _{Pt})	Specific activity (mA/cm ² _{ECSA})
Pt NTAs	0.1327	158.2	0.55
Ni@Pt NTAs	0.0562	249.3	0.88
Ni@Pt@Ni@Pt NTAs	0.0965	362.7	1.34
Pt@Ni@Pt NTAs	0.0920	228.3	0.84
Pt@Ni@Pt@Ni@Pt NTAs	0.1505	315.0	1.20