Supplementary Information

Pt-Ni alloyed nanocrystals with controlled archtectures for enhanced methanol oxidation

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Experimental

Chemicals. Pt(acac)₂(acac: aceylacetonate), nickel acetate (Ni(ac)₂), 1,2–tetradecanediol (TDD), was from J&K Chemical Ltd. Oleylamine (OAm, 80-90 wt%) and 1-octadecene(ODE) were purchased from Aladdin. Nafion (5 wt%) was purchased from Sigma-Aldrich. Oleic acid (OA), hexane (\geq 97 wt%), ethanol (\geq 99.7 wt%), HClO₄ (\approx 70–72 wt%), were commercially available from the Shanghai Chemical Reagent Co. Ltd. *Synthesis of Pt-Ni alloyed multi-arms.* The synthesis was carried out using standard airless procedures. 0.05 mmol of Pt(acac)₂, 0.05 mmol of Ni(AC)₂, 0.5 mmol of TDD, 0.6 mL OA and 0.9 mL OAm were mixed together with 5 mL ODE in a 25 mL three-neck flask under an nitrogen stream at room temperature. The mixture was then heated to 120 °C with vigorous stirring. The mixture turned into a transparent yellow-green color. After 20 min, the mixed solution was subsequently heated to 230 °C at a heating rate of 10 °C/min and maintained at this temperature for 30 min. The black colloids was cooled down to room temperature by quickly removing the heating source, and then isolated by adding a sufficient amount ethanol followed by centrifugation at 13000 *rpm* for 15 min. After washed for several times to remove surfactants, the product was redispersed in hexane for further characterization.

Synthesis of Pt-Ni alloyed nanoflowers. Change the amount of the amount of OAm to 3.6 mL and react at 230 °C for 5 min, and the other condition are same with the method above.

Electrochemical measurement. The electrochemical measurements were carried out with a three-electrode system on an IM6ex electrochemical workstation (Zahner, Germany). A platinum foil and Ag/AgCl (3.5 M) were used as the counter and reference electrodes, respectively. A glassy-carbon rotating disk electrode (RDE) (PINE, 5 mm diameter, 0.196 cm⁻²) was polished to a mirror finish and thoroughly cleaned. To prepare the working electrode, alcohol suspensions of 0.5 mg of catalyst (recorded with metal Pt) per milliliter with 0.02 wt% Nafion (diluted from 5 wt% Nafion, Sigma–Aldrich) were obtained by ultrasonic mixing for about 30 min. The metal-catalyst ink was transferred onto the RDE and dried at room

temperature. Prior to each experiment, the electrode potential was cycled between -0.214 to 0.8 V vs Ag/AgCl with a scan rate of 250 mV s⁻¹ until a stable voltammogram was obtained in 0.1 M HClO₄ solution. After potential cycling, the sweep rate was changed at 50 mV s⁻¹ from -0.214 to 1.0 V vs Ag/AgCl for ECSA measurement. The methanol oxidation reaction was conducted in Ar-saturated 0.1 M HClO₄ and 1.0 M MeOH solution at the sweep rate of 50 mV s⁻¹ at the room temperature.

Characterization. The samples were characterized by powder X-ray power diffraction (XRD), using a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite monochromaticized Cu K α radiation ($\lambda = 1.54056$ Å). The transmission electron microscope (TEM), energy dispersive spectrometer (EDS) and high-resolution transmission electron microscope (HR-TEM) images and scanning transmission electron microscopy energy dispersive spectrometer (STEM EDS) element mapping were obtained using a JEOL-2010F TEM instrument with an acceleration voltage of 200KV. Inductively coupled plasma (ICP) datas were obtained using an Optima 7300 DV instrument. Electrochemical measurements were performed using an IM6ex electrochemical workstation (Zahner, Germany). The X-ray photoelectron spectra (XPS) were recorded on an ESCALab MKII X-ray photo-electron spectrometer using Mg Ka radiation exciting source.



Fig. S1 XRD patterns of Pt-Ni multi-arms and flowers.



Fig. S2 Energy-disperse X-ray spectra (EDS) of the obtained Pt-Ni multi-arms (a) and flowers (b).



Fig. S3 TEM images of the products: (a) when the solution color changes from brown to dark; (b) after 5 min.



Fig. S4 TEM image of the obtained Pt multi-arms without addition of the Ni precursor.



Fig. S5 TEM images of products without adding OA when (a) OAm is 0.9 mL; (b) OAm is 3.6 mL.



Fig. S6 TEM images of the products with different ratios of OAm/OA after 5min: (a)2/1; (b) 4/1; (c) 8/1. (d),(e),(f) are the corresponding EDS results of (a),(b),(c).



Fig. S7 TEM images of carbon-supported Pt-Ni multi-arms (a) and flowers (b) catalysts.



Fig. S8 (a) Cyclic voltammograms of Pt-Ni multi-arms, Pt-Ni nanoflowers, Pt multi-arms and commercial Pt/C catalysts recorded in N_2 -saturated 0.1 M HClO₄ solution at a sweep rate of 50 mV s⁻¹. (b) The XPS spectra of the samples.