Electronic Supplementary Information

Solvent-controlled Platinum Nanocrystals with High Growth Rate along ⟨100⟩ to ⟨111⟩ and Enhanced Electro-active in Methanol Oxidation Reaction

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Experimental details:

All chemicals were analytical grade and used as received without further purification. In a typical synthetic approach, 5.0 mLof glycerol, 8.0 mg of Pt(acac)$_2$, 20.0 mg of polyvinyl pyrrolidone (PVP, MW=30000), and benzoic acid (5.0 mg) were added to the mixture of 5.0 mL of chloroform and 5.0 mL of glycerol (or 10.0 mL of water or the mixture of 5.0 mL of water and 5.0 mL of glycerol), followed by vigorous stirring for 10 min. The resulting homogeneous solution was transferred into a 30-mL Teflon-lined stainless-steel autoclave. The sealed vessel was then heated at 180^{o}C for 12 h before it was cooled down to room temperature. The obtained products were separated from the reaction solution and washed three times with the mixture of ethanol and acetone to remove any excess surfactants via centrifugation at 10000 rpm for 10 min, and then dried in oven for further characterization.

Electron microscope specimens were prepared by dispersing the suspension of obtained Pt products and drop-casting it onto copper grids. Transmission electronic microscopy (TEM) and high-resolution TEM (HRTEM) images were recorded on a FEI Tecnai G^2 F20 S-TWIN field emission microscope equipped with a Gatan CCD camera at an accelerating voltage of 200 kV. UV−vis diffuse reflectance spectra were recorded at room temperature in air on a SPECORD.50 spectrophotometer.

6.0 mg of the as-obtained Pt particles in typical synthesis (or commercial Pt particles) were added into 0.5 mL Nafion solution (0.5 wt.%) to form a uniform suspension at magnetic stirring for 60 min. The suspension was spread on the glassy carbon electrode (GCE), and then dried for 30 min at 75^{o}C. The amount of catalyst on the electrode was controlled such that Pt loading was maintained as 2.0 mg·cm^{-2}. All electrochemical measurements were performed on AutoLab PGSTAT302N electrochemical workstation equipped with SCAN250 module. A conventional three-electrode glass cell was used with a platinum wire as the counter electrode, and an Hg|Hg$_2$Cl$_2$ electrode with saturation KCl solution (SCE) was used as the reference electrode for all the potentials reported herein. Double-distilled water was used throughout.

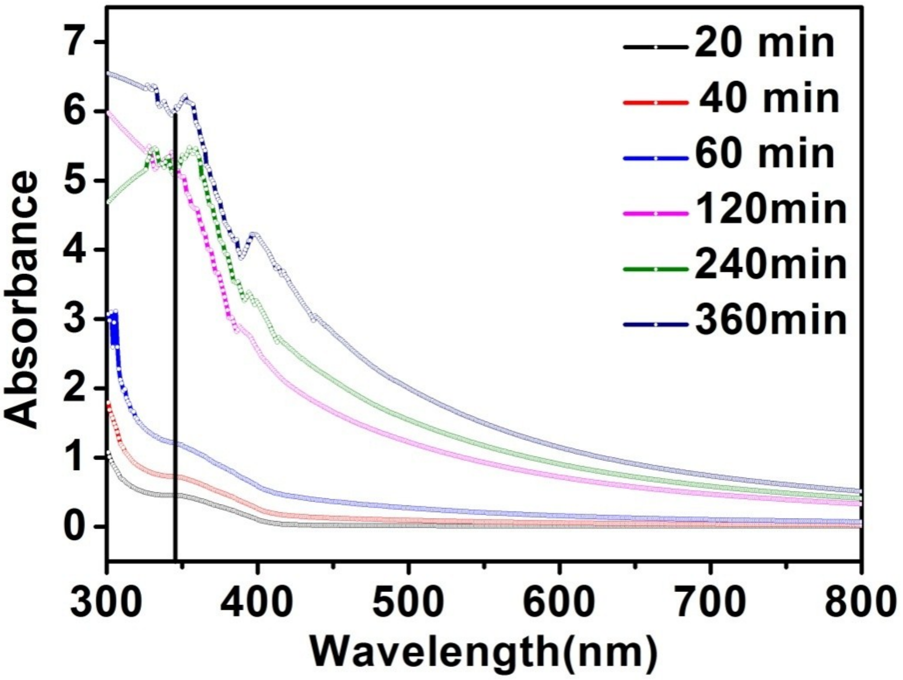

Fig. S1 UV−vis spectra of the time evolution of substrate concentration for as-obtained polyhedral nanocrystals in typical synthesis with glycerol-water as solution.

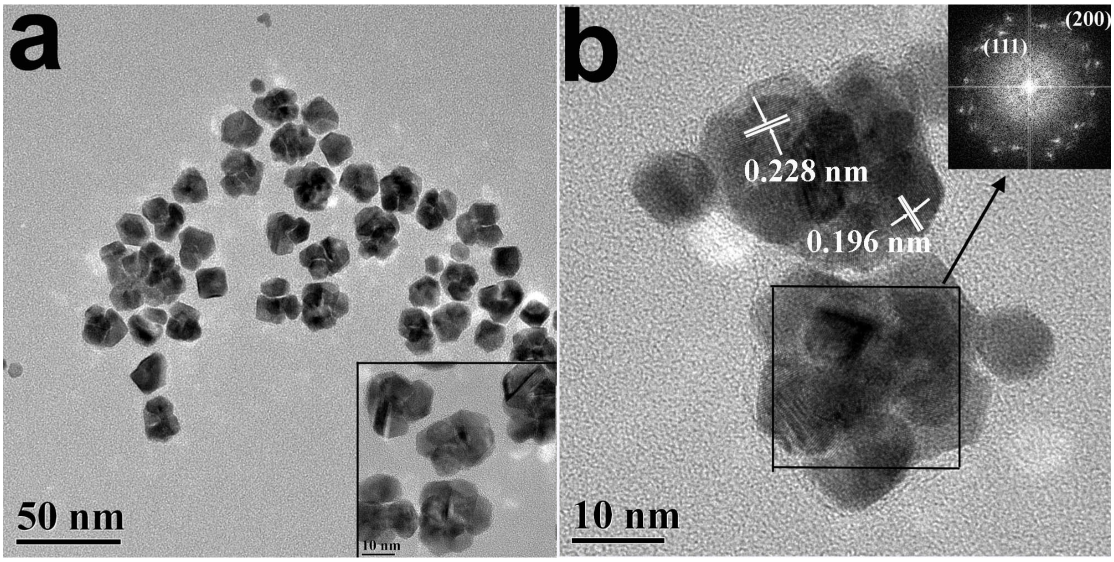

Fig. S2 TEM image (a), HRTEM images (b), and corresponding FFT image (inset of b) of as-obtained Pt multipolyhedral nanostructures in typical synthesis with the mixture of ethylene glycol and water as solution.

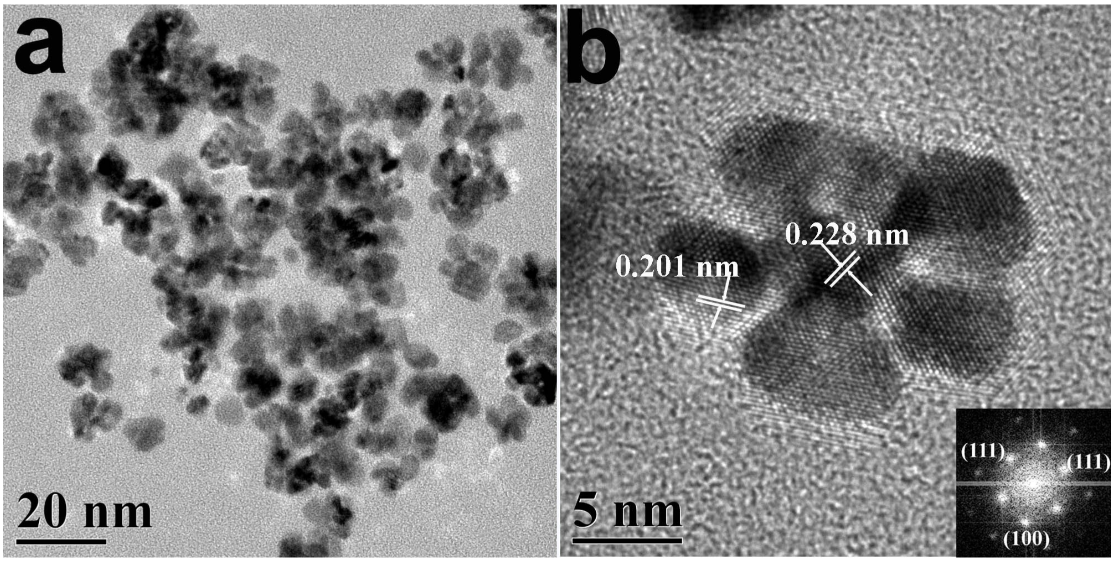

Fig. S3 TEM image (a), HRTEM images (b), and corresponding FFT image (inset of b) of as-obtained flower-like Pt nanostructures in typical synthesis (glycerol-water mixture) with oxalic acid substitution for benzoic acid.

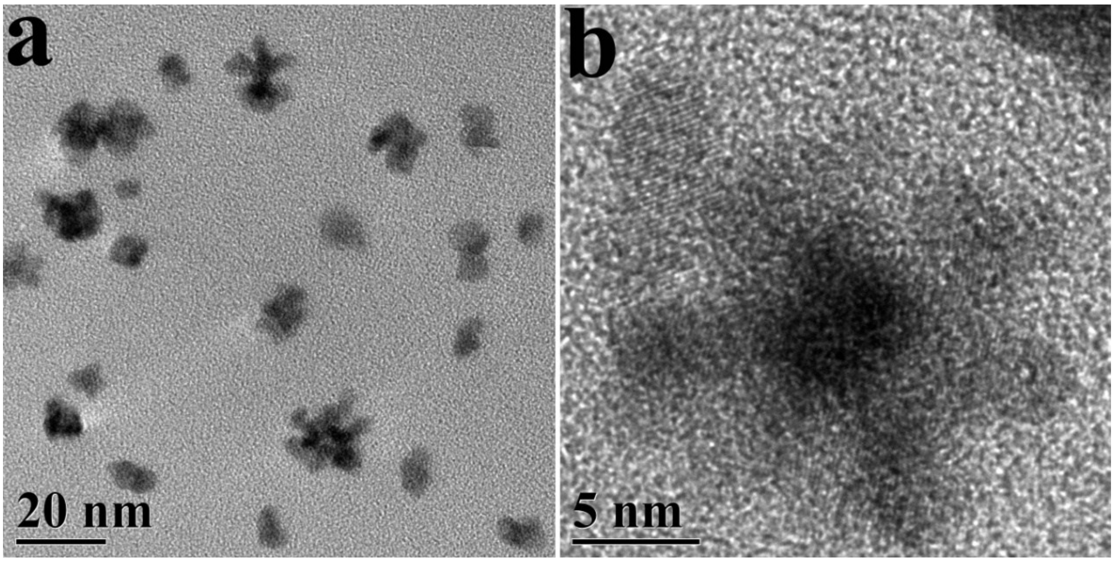

Fig. S4 TEM image (a) and HRTEM images (b) of as-obtained Pt nanostructures in typical synthesis (glycerol-chloroform mixture) with temperature of 200^{o}C.

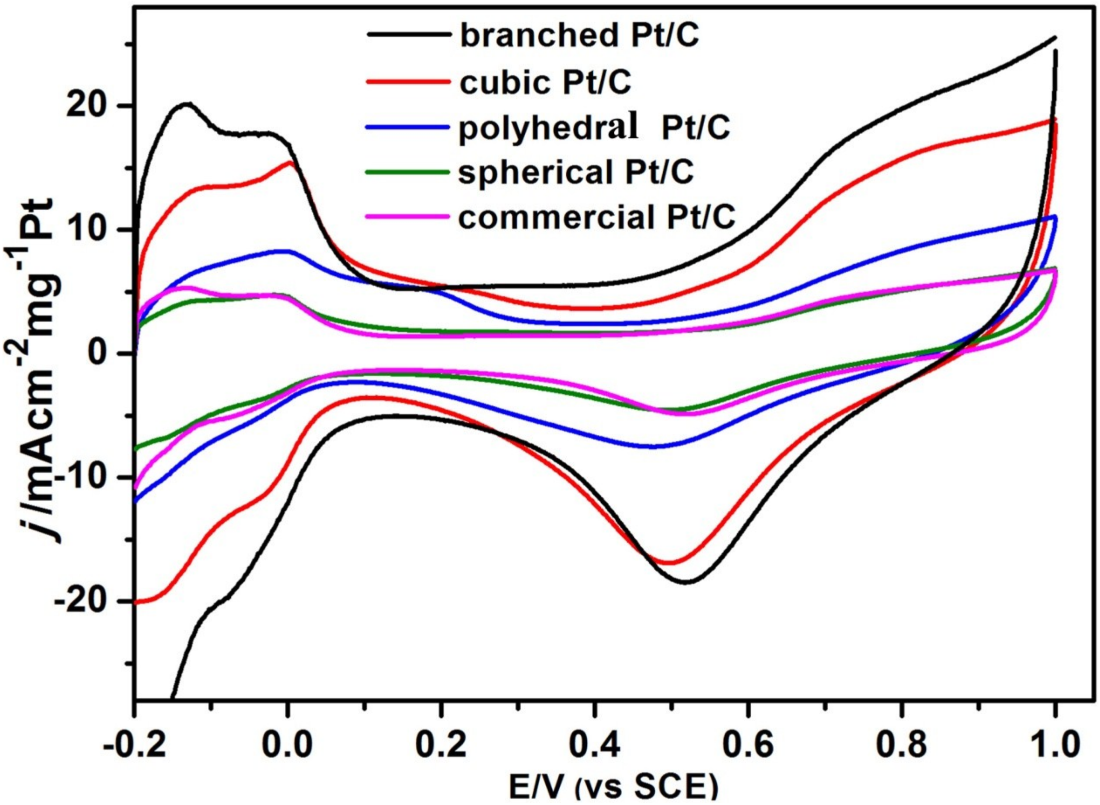

Fig.S5 Cyclic voltammetric curves of Vulcan XR-72 loaded with as-obtained four different shaped Pt nanocrystals and commercial Pt nanoparticles in 0.5 M H_2SO_4 with a sweep rate of 50 mV·s^{-1}.

Table S1 The electrochemically active surface area (ECSA) calculated by the cyclic voltammetric curves (Fig. S5) of Vulcan XR-72 loaded with as-obtained four different shaped Pt nanocrystals and commercial Pt nanoparticles.

Type of Pt/C catalyst	**ECSA/m^{3}·g^{-1}Pt**
branched Pt/C	62.2
cubic Pt/C	47.8
polyhedral Pt/C	26.1
spherical Pt/C	15.2
commercial Pt/C	14.2