

Supplementary Information for

Carbon monoxide-controlled synthesis of surface-clean Pt nanocubes with high electrocatalytic activity

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Experimental Details

Reagents: The syntheses were carried out using commercially available reagents. Platinum (II) acetylacetonate [Pt(acac)₂, Pt 48.0% min] was purchased from Alfa Aesar, Oleylamine (OAm, 80-90%) from Acros Organics, Oleic acid (OLA) from Guangdong Xilong Chemical Co. Ltd. PVP (K30, AR), benzyl alcohol, n-butylamine from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Carbon nanotubes (CNTs) were purchased from Shenzhen Nanotech Port Co. Ltd (NTP, Shenzhen, China). Cerium dioxide and P25 were purchased from Sigma Aldrich and Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China), respectively. CO (99.99%) was purchased from Linde Gas. All chemicals were used as received without further purification.

Surfactant-free synthesis of Pt nanocubes on different supports: In a typical synthesis of Pt nanocubes, Platinum(II) acetylacetonate (20 mg), support (e.g., CNTs, CeO₂ or P25) (50 mg) were mixed together with 10 mL benzyl alcohol in a glass pressure vessel. The resulting mixture after stirring at room temperature for 5 min was charged with CO to 1 bar and then heated in oil bath which was preheated to 180°C for 3 h with vigorous stirring. The resulting products were collected by centrifugation, and washed several times with ethanol.

Synthesis of Pt nanocrystals on CNTs in the presence of PVP (Pt NC-CNTs-PVP): In a typical synthesis of the Pt NPs-CNTs-PVP, Platinum(II) acetylacetonate (20 mg), poly(vinylpyrrolidone) (K30, 320.0 mg), Carbon nanotubes (50 mg) were mixed together with 10 mL benzyl alcohol in a glass pressure vessel. The resulting mixture after stirring at room temperature for 5 min was charged with CO to 1 bar and then heated in oil bath which was preheated to 200°C for 1.5 h with vigorous stirring. The resulting products were collected by centrifugation, and washed several times with ethanol and acetone.

Synthesis of Pt nanocrystals on CNTs in the presence of Oleylamine (Pt NC-CNTs-OAm): In a typical synthesis, Platinum(II) acetylacetonate (20 mg) was dissolved in a mixed solvent of 2 mL OAm and 8 mL OLA in 70°C oil bath for 10min. The resulting homogeneous solution was transferred to a glass pressure vessel. After being charged with CO to 2 bar, the vessel was heated at 180°C for 40 min with vigorous stirring. After being precipitated by 35 mL ethanol, the products were re-dispersed in 25 mL n-butylamine which contained 50 mg CNTs.¹ After being stirred at room temperature overnight, the Pt NC-CNTs-OAm catalysts were washed several times with ethanol and separated via centrifugation.

Characterization: TEM (including high-resolution transmission electron microscopy, HRTEM) studies were performed on a TECNAI F-30 high-resolution transmission electron microscopy operating at 300 kV. The samples were prepared by dropping ethanol dispersion of samples onto 300-mesh carbon-coated copper grids and immediately evaporating the solvent. SEM studies were performed on a S4800 scanning electron microscopy with a field emission electron gun. The samples were prepared by dropping ethanol dispersion of samples onto Si substrate and immediately evaporating the solvent. X-ray diffraction (XRD) measurements were recorded on a PANalytical X'pert PRO diffractometer using Cu K α radiation, operating at 40 kV and 30 mA. Electrochemical measurements were carried out on a CHI760D electrochemical workstation (CH Instrument Co., USA).

Electrochemical Measurements: To obtain the working electrodes, ethanol dispersion of purified catalysts were first deposited on a glassy carbon electrode. After the ethanol was dried, 2 μ L of 0.1 wt% Nafion solution was dropped on the electrode surface to stabilize the catalysts on the electrode surface. A saturated calomel electrode (SCE) and a platinum foil were used as the reference and counter electrode, respectively. Before methanol electrooxidation measurement, cycles of potential sweeps between -0.25V and 1.2V at a sweep rate of 100 mV/s were applied until the maximum electrochemical surface area (ECSA) was got. For the methanol electrooxidation, the cyclic voltammograms were recorded at a sweep rate of 50 mV/s in an aqueous solution of 0.5 M H₂SO₄ and 1 M methanol. Chronoamperometric curves for methanol oxidation were recorded at 0.6V.

Computational details: All calculations were performed by using the Vienna ab initio simulation package (VASP).^{2, 3} Exchange and correlation were treated within the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA).^{4, 5} The cutoff energy for the plane-wave expansion was set to be 400 eV, which is believed to give well-covered total energies and structures. The Pt (100) and Pt (111) surfaces were

modeled by a 2×2 supercell with a five-layer slab and a vacuum region of more than 30 Å thickness. During structural optimization, the bottom three layers of the slab were fixed at bulk truncated position, while the top two layers and the adsorbates were fully relaxed. For simplification, CO was placed on top sites over the surfaces. The k-points sampling were generated following the Monkhorst-Pack procedure with a 5×5×1 mesh. Calculations for the free gas-phase molecules were performed in a 20×20×20 Å³ unit cell and the Brillouin zone was sampled by single k point.

The adsorption energy (E_{ads}) was defined as

$$E_{\text{ads}} = E_{\text{slab/mole}} - E_{\text{slab}} - E_{\text{mole}} \quad (1)$$

in which $E_{\text{slab/mole}}$ is the energy of the slab with adsorbates; E_{slab} is the energy of the slab, and E_{mole} is the energy of gas-phase molecular. Similar to Tang's work,⁶ the surface energy (ϕ) for a give clean surface is calculated by

$$\phi_{\text{surf}} = [(E_{\text{slab}} - nE_{\text{bulk}}) - (E_{\text{prim}} - nE_{\text{bulk}})] / 2N_{\text{surf}} \quad (2)$$

where E_{bulk} is the energy of a bulk unit cell; E_{prim} is the energy of the slab as mentioned above but without any relaxation, i.e. all atoms frozen in bulk-truncated positions. N_{surf} is the number of the surface Pt atoms in the slab and n is a factor which equal to the atoms in slab unit cell divide by the atoms in bulk unit cell. For the surface covered by adsorbates, ϕ is calculated as:

$$\phi_{\text{ads}} = \phi_{\text{surf}} + E_{\text{ads}} \quad (3)$$

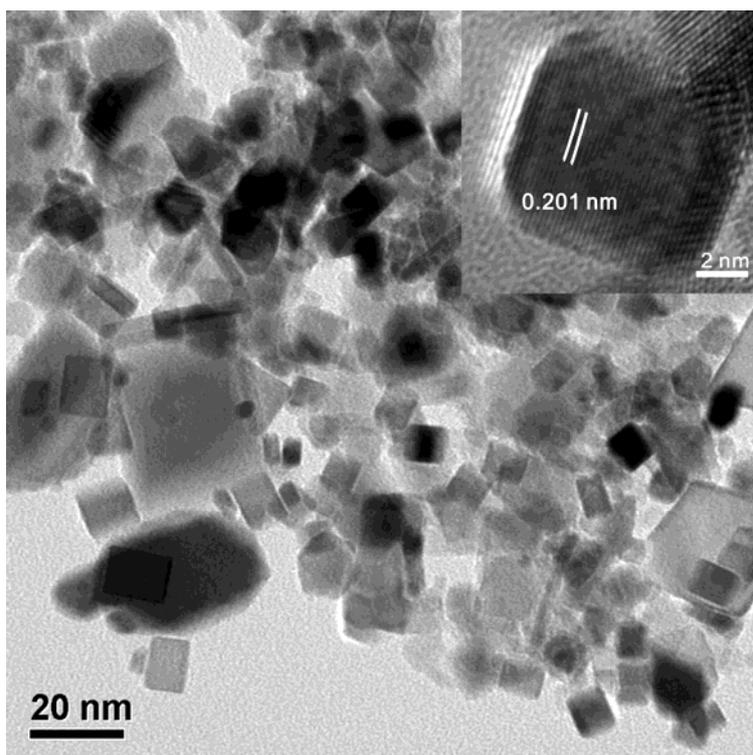


Figure S1 TEM images of Pt nanocubes supported on CeO₂.

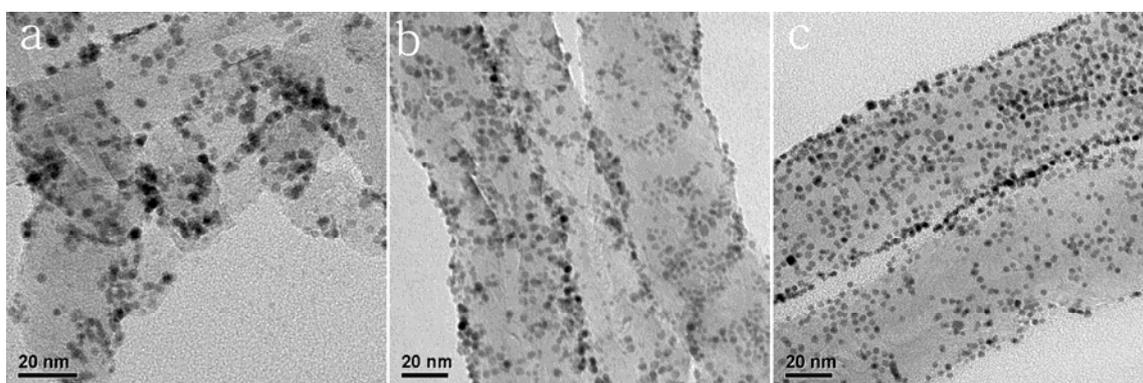


Figure S2 TEM images of the Pt NPs-CNTs synthesized with different CO partial pressure (a) 0 bar, (b) 0.05 bar and (c) 1 bar.

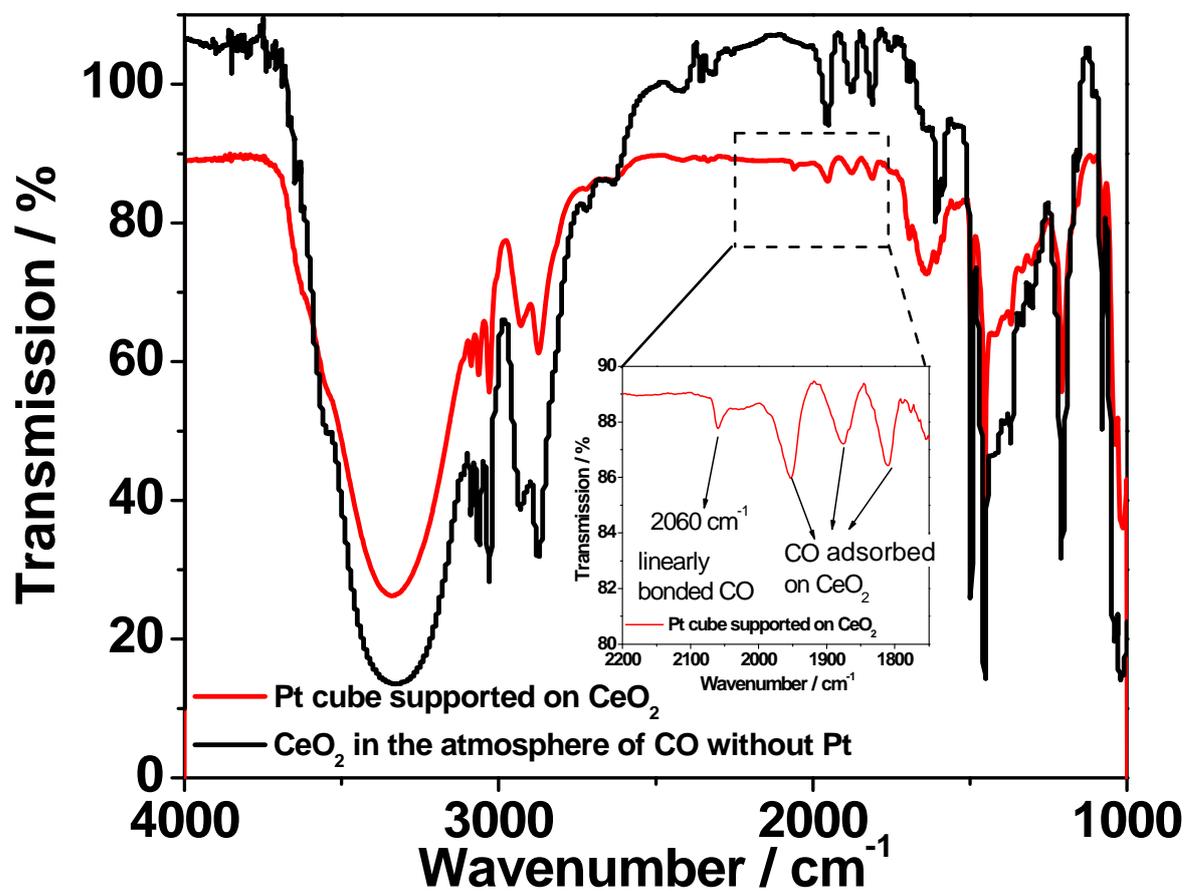


Figure S3 Fourier transform IR (FT-IR) spectroscopy characterization for the as-prepared Pt nanocubes.

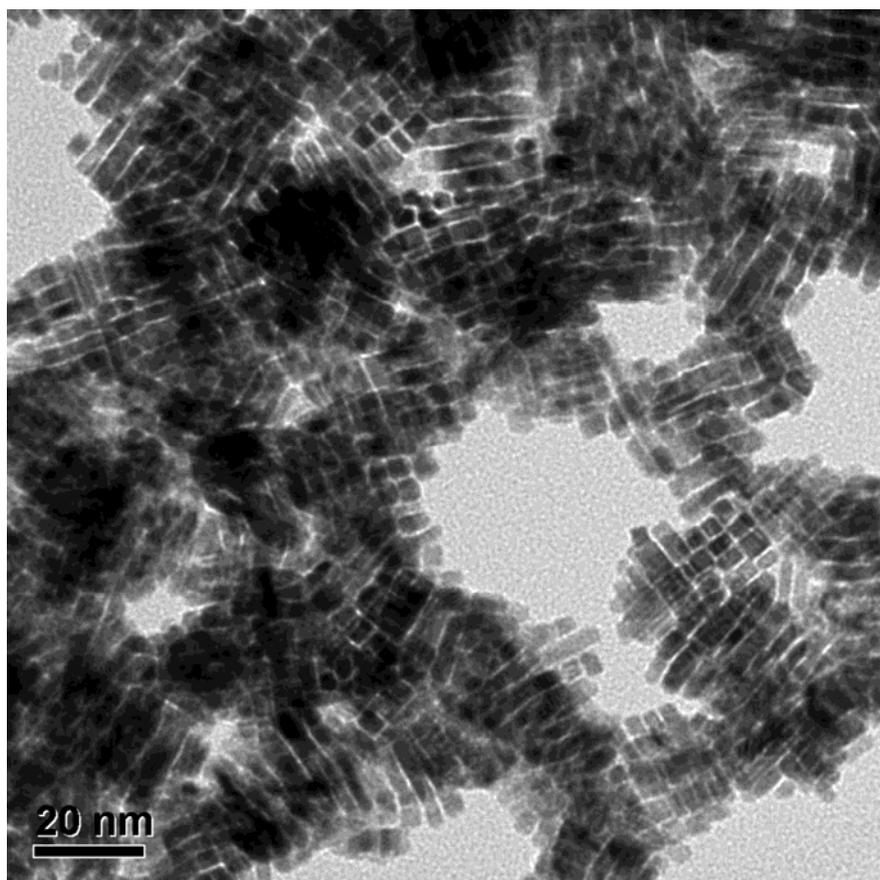


Figure S4 TEM images of Pt nanocrystals synthesized without the use of supports.

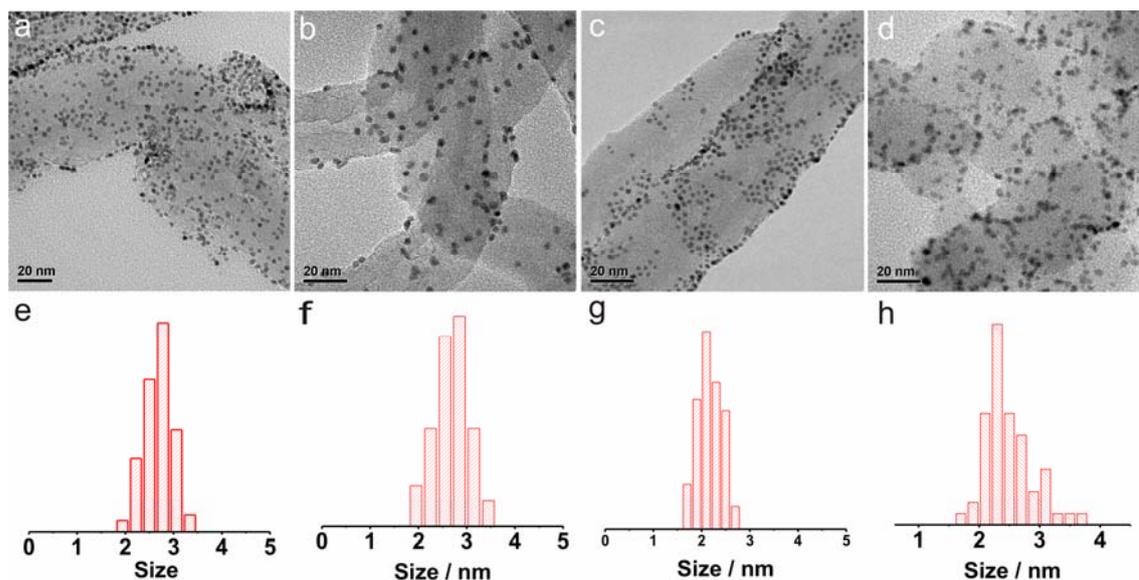


Figure S5. (a-c) the TEM images of Pt NPs-CNTs synthesis with no surfactant, PVP, oleylamine and (d) commercially available Pt/C. (e-f) the size distributions corresponding to the images of (a-d).

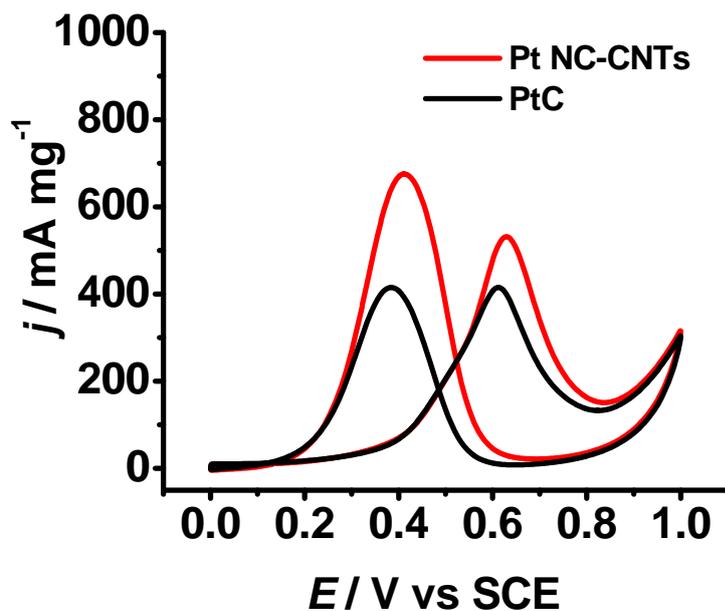


Figure S6. Cyclic voltammograms for methanol oxidation reactions catalyzed by Pt NC-CNTs and commercially available Pt/C, respectively, in an aqueous solution of 0.5 M H_2SO_4 with 1 M methanol.

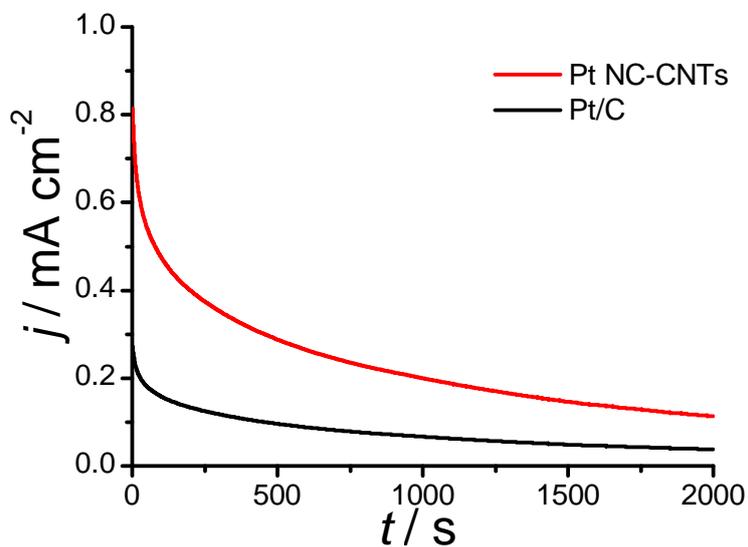


Figure S7 Chronoamperometric curves recorded at 0.6 V.

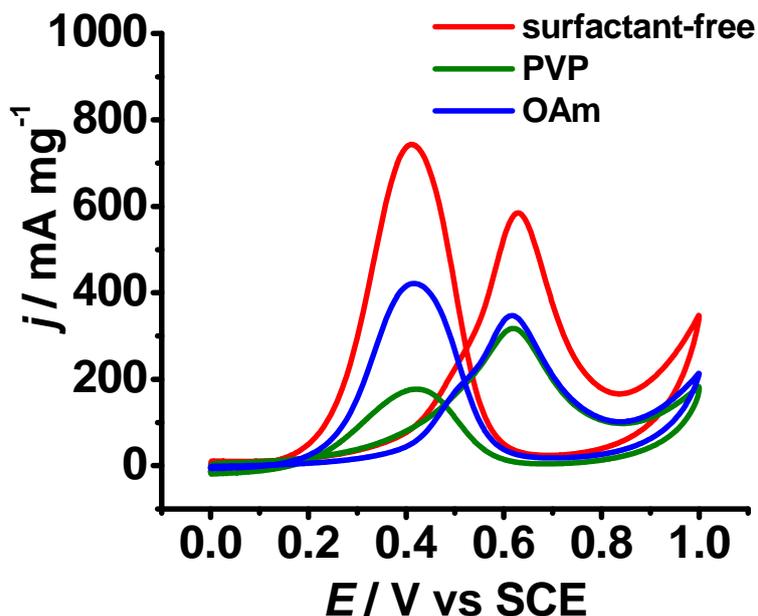


Figure S8 Cyclic voltammograms for methanol oxidation reactions catalyzed by Pt nanocrystals (synthesis with or without surfactant) supported on CNTs, respectively, in an aqueous solution of 0.5 M H_2SO_4 with 1 M methanol.

Reference:

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