

## CO-Assisted Synthesis of Finely Size-Controlled Platinum Nanoparticles

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### Electronic Support information (E.S.I.).

### Experimental Section

*Preparation of size-dependent Pt clusters:* Carbon black ( $S_{\text{BET}} = 236 \text{ m}^2/\text{g}$ , Vulcan XC-72, Carbot) was pre-treated in concentrated  $\text{HNO}_3$  (65%, ACROS) with magnetic stirring at 100 °C for 8 h and then rinsed with deionized water. A suspension of pre-treated Vulcan XC-72 and  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  (99.9%, ACROS), equivalent to a 20% weight ratio of Pt to C, was mixed with deionized water and stirred for 2 h. The pH of the suspension was adjusted by the addition of concentrated  $\text{NH}_4\text{OH}$  solution. A gas stream with a fixed CO/Ar ratio was introduced through an aerated filter into the  $\text{NaBH}_4$  solution for 15 min. (Caution! CO is highly toxic and should be handled using appropriate protective equipment. The use of effective ventilation, such as a fume hood, is essential). The suspension was immediately injected into the aerated  $\text{NaBH}_4$  solution with magnetic stirring (900 rpm). After 1 h, the synthesized samples were centrifuged and rinsed with water. The synthesized samples prepared at various CO/Ar ratios, referred to as: CO-0%, CO-25%, CO-50%, CO-75%, and CO-100%, were collected after air-drying at 80 °C; they were not subjected to any further purification. The PVP-protected Pt/C NPs were synthesized in the presence of 1 M or 2 M PVP ( $M_w$ : 55,000; ACROS) using the procedure described above, but without introducing CO into the reaction solutions; they are referred to as PVP-1M and PVP-2M, respectively.

*Characterization:*

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES; JY2002-2, HORIBA) was used to evaluate the metal loading of Pt, based on the weight of XC-72 (Table 1). After reaction, the residual solution was collected via the centrifugation of the suspension. The metal loading was estimated by the Pt ion concentration detected in the residual solution.

X-ray diffraction (XRD, Rigaku, Dmax-B X-ray diffractometer, Japan) was performed using a Cu K $\alpha$  radiation source operated at 40 kV and 100 mA. A scan rate of 0.05 deg s<sup>-1</sup> was employed for values of  $2\theta$  between 20° and 90°.

TEM (F20-G2, Philips/Tecnai) images were obtained using an accelerating voltage of 200 KV. Prior to the HRTEM measurements, the sample solution was prepared by suspending the homemade catalysts in absolute ethanol solution with ultrasonication. A drop of the sample specimen was applied onto the carbon-supported copper grid and the grid was placed in a vacuum oven at 25 °C overnight.

X-ray photoemission spectroscopy (XPS, Scientific Theta Probe, Thermo/VG), with an Al<sub>K</sub> source, performed at an energy of 1486.6 eV, operating at 15 kV and 100 W, was used to confirm the electronic state of the synthesized Pt clusters (Pt-4f<sub>5/2</sub> and Pt-4f<sub>7/2</sub>) on carbon black. The sputtered Au on the half side of the sample pellet was employed as an internal standard for energy correction.

X-ray absorption spectra were recorded at the Taiwan beamline BL12B2 in Spring-8, Hyogo, Japan. The electron storage ring of Spring-8 was operated at 8 GeV. A double-crystal Si(111) monochromator was employed for energy selection with a resolution ( $\Delta E/E$ ) of  $1 \times 10^{-4}$  at the Pt-L<sub>III</sub> edge (11,564 eV). An appropriate amount of catalyst powder was pelletized in a stainless-steel mold (1 cm  $\times$  4 cm) to reach the optimum absorption thickness ( $\Delta\mu\chi = \text{ca. } 1.0$ ; where  $\Delta\mu$  is the absorption edge and  $\chi$  is the thickness of the pelletized sample); the mold was placed into a sealed stainless-steel gas chamber. To completely eliminate the oxide

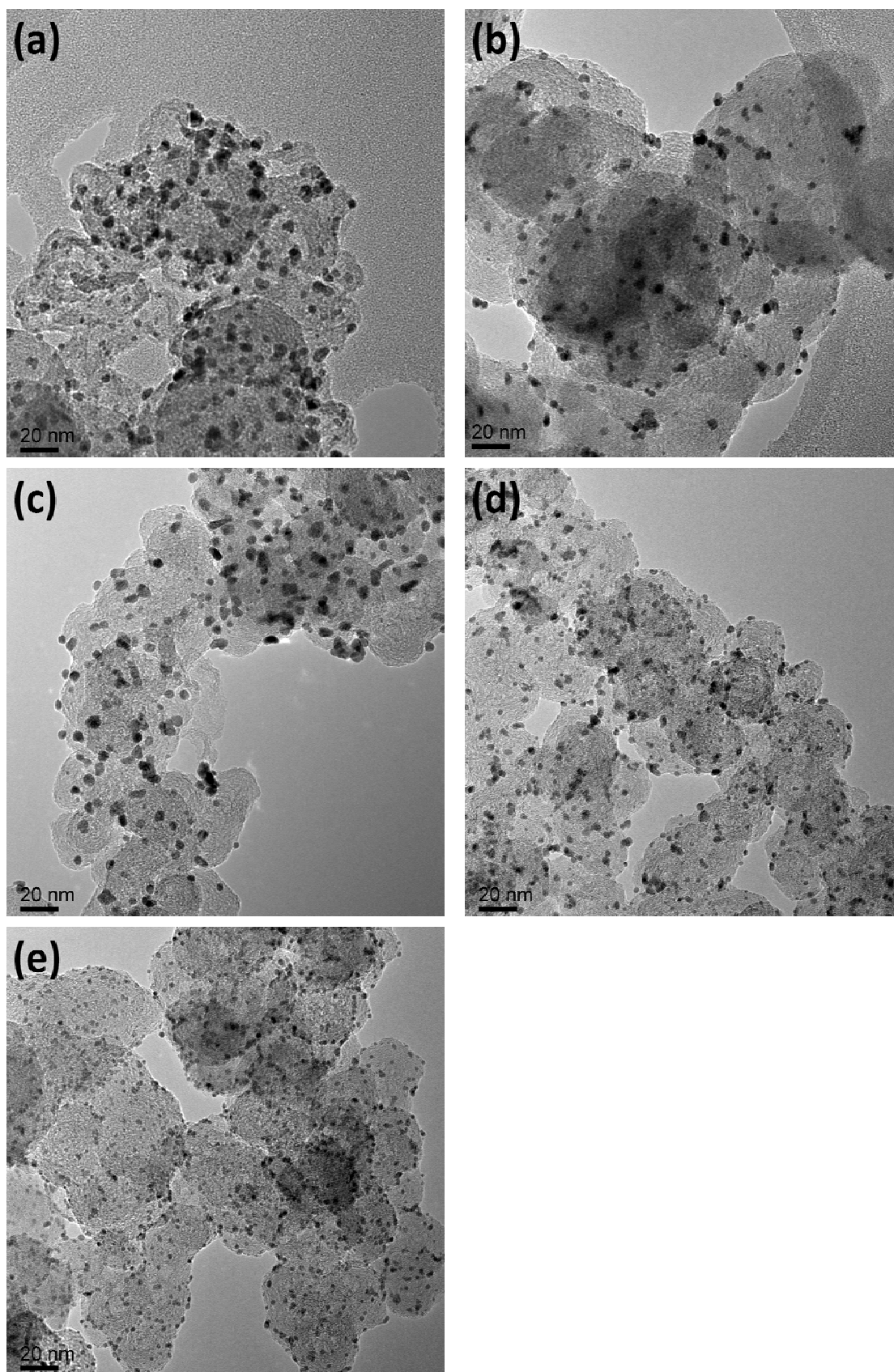
contribution, the pelletized sample was exposed to a mixed stream of 10% H<sub>2</sub> and 90% N<sub>2</sub> for 1 h prior to XAS measurement. All spectra were recorded in transmission mode at room temperature; the high harmonic effect was eliminated by detuning the double-crystal Si (111) monochromator. All ionization chambers were placed in series to measure the intensities of the incident beam ( $I_0$ ), the beam transmitted by the sample ( $I_t$ ), and the beam subsequently transmitted by the reference foil ( $I_r$ ). The EXAFS function,  $\chi$ , was obtained by subtracting the post-edge background from the overall absorption coefficient and then normalizing to the edge jump. The normalized function,  $\chi(E)$ , was then converted to  $k$ -space, which is the photoelectron wave vector. The wave vector function  $\chi(k)$  was weighted by  $k^2$  to compensate for the damping of the backscattering oscillation in the high- $k$  region. Subsequently,  $k^2$ -weighted  $\chi(k)$  data ranging from 3.20 Å<sup>-1</sup> to 13.45 Å<sup>-1</sup> at the Pt-L<sub>III</sub> edge were converted to “ $r$ ” space through Fourier transformation to identify the coordination shell.

*CO anodic stripping cyclic voltammetry:* A conventional three-electrode electrochemical cell was used for all electrochemical measurements. Pt foil and a saturated calomel electrode were used as the counter electrode and reference electrodes, respectively, powered by a potentiostat/galvanostat (Potentiostat-1480, Solartron). All potentials in were referred to the reversible hydrogen electrode; all measurements were performed at 25 ± 1 °C. A weighed amount of catalyst powder was suspended ultrasonically in a mixture of absolute EtOH (0.45 mL) and 5 wt % Nafion solution (0.05 mL) for 2 hours. Catalyst ink (7 µL, containing 14.0 µg Pt) was then micropipetted onto a glassy carbon electrode (geometric area: 0.1964 cm<sup>2</sup>) and subsequently dried at ambient temperature until a uniform thin film was formed. The working electrode was immersed in CO-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> for 15 min. After forming a saturated CO adlayer on the electrode, the electrolyte was purged with N<sub>2</sub> for 30 min to remove residual CO from the electrolyte. The CO stripping data were recorded in CO-free solution by sweeping the potential from 0.05 to 1.1 V at a scan rate of 5 mV s<sup>-1</sup>. The ECSA, based on the weight of Pt (m<sup>2</sup> g<sub>Pt</sub><sup>-1</sup>) was determined by integrating the CO stripping area of the cyclic

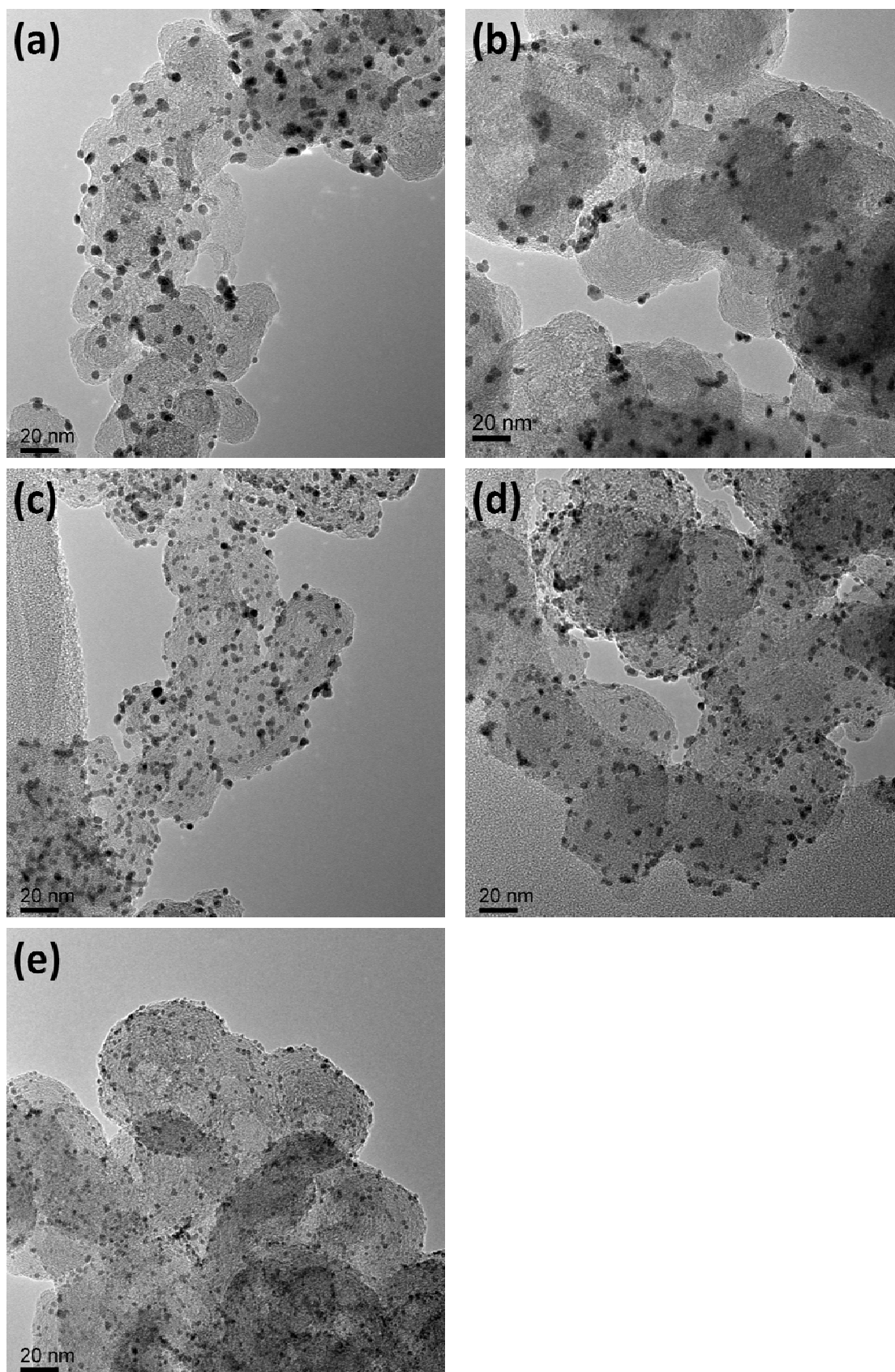
voltammogram. The integrated area was divided by the scan rate ( $5 \text{ mV s}^{-1}$ ) and  $4.2 \text{ Cm}^{-2}_{\text{Pt}}$ , which represent the number of coulombs required for the oxidation of a CO monolayer adsorbed on a Pt surface. The MOR currents for all the nanocatalysts were recorded in  $\text{N}_2$ -saturated 1 M methanol- sulphuric acid solution. The linear sweep started from 0.2 V to 0.9 V at a scan rate of  $5 \text{ mV s}^{-1}$  and the rotating speed was 900 rpm.

## Results and Discussion

TEM images in **Fig. S1**, were taken from duplicates of the synthesized Pt/C nanoparticles. Table 1 showing a comparison of the mean sizes and mean metal loadings of the synthesized Pt/C, reveals a decreasing size tendency with an increase in the CO/Ar ratio. Where the samples were prepared with the CO/Ar ratio exceeding 75 %, uniform spherical NPs can be observed with a narrow size distribution from 1 to 2 nm (**Fig. S1d-e, 2d-e**). PVP employed in this work plays the same function as a stabilizer in the highlighted literature.<sup>S11-3</sup> TEM images of the PVP-stabilized Pt/C NPs show that the average diameter ranges from 3 to 4 nm and shows that Pt NPs agglomerate to form a dendrite-like morphology (**Fig. S3a-b**).

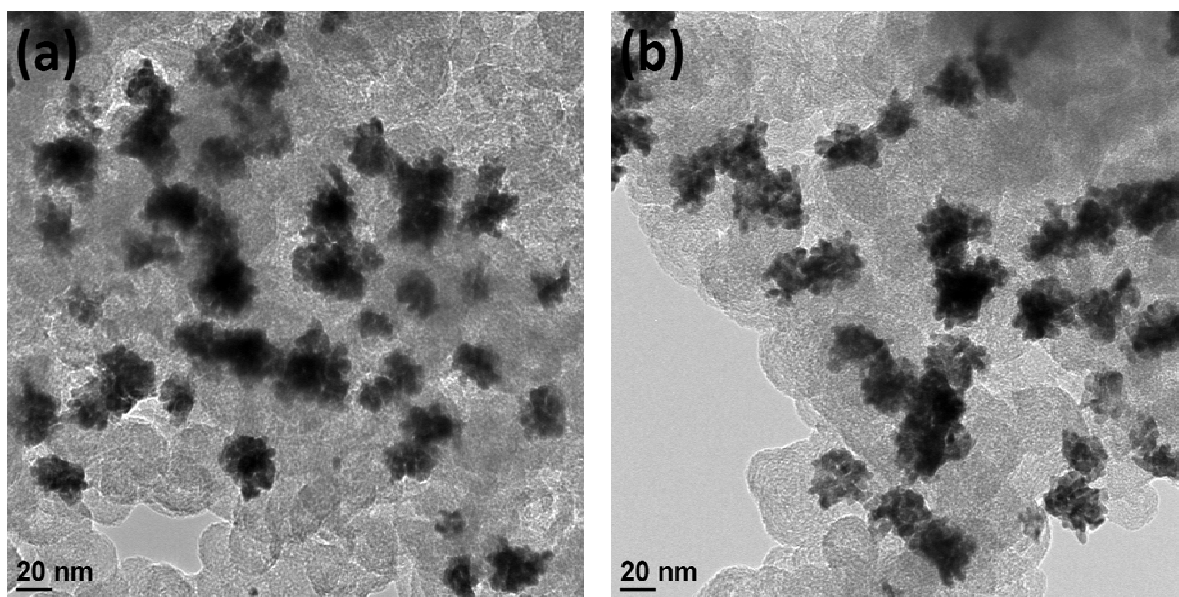


**Fig. S1** TEM images of (a–e) Pt/C NPs synthesized at various CO/Ar ratios ( duplication # 1 )(a:0%; b: 25%; c:50%; d:75% ; e:100%).



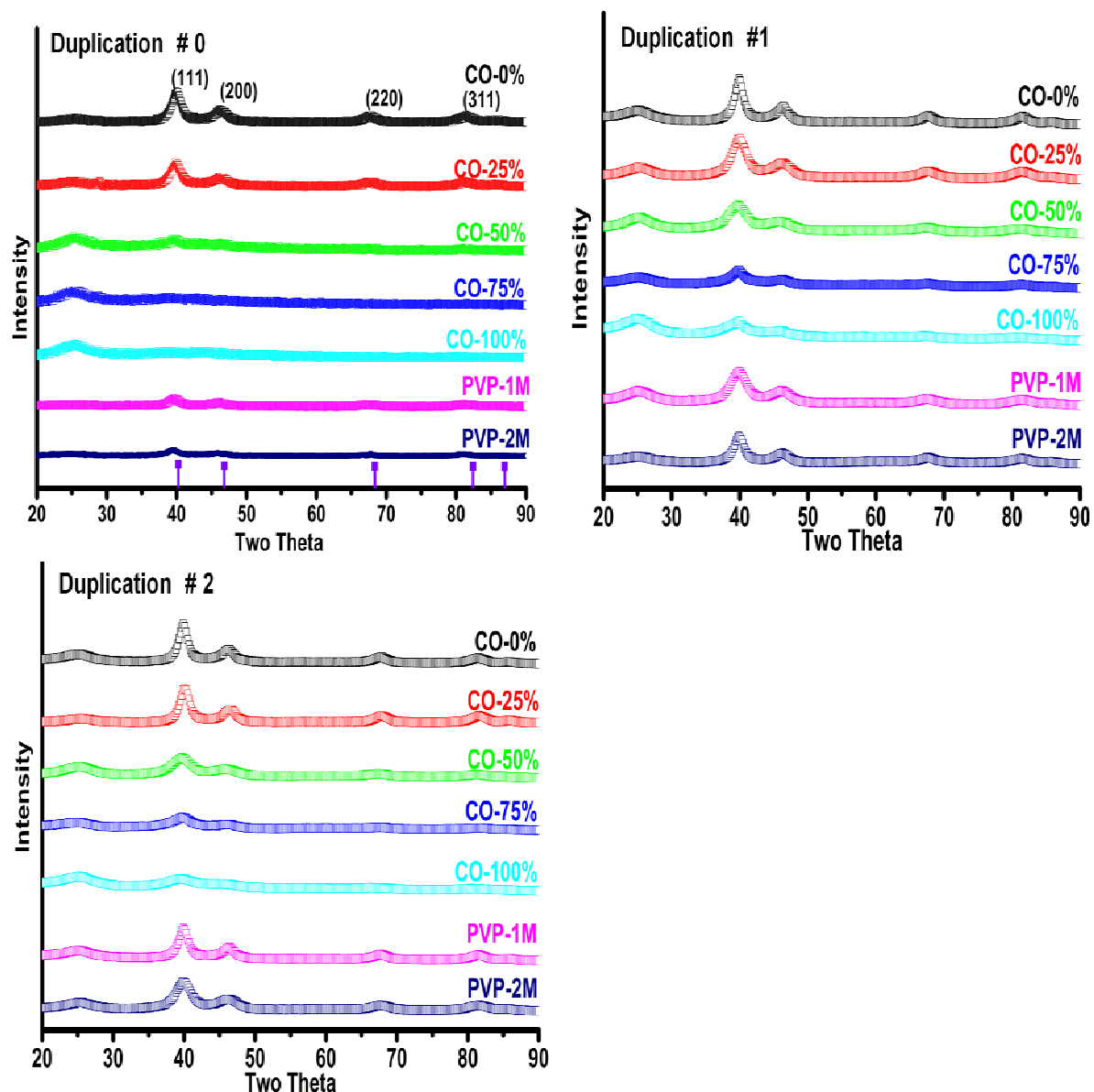
**Fig. S2** TEM images of (a–e) Pt/C NPs synthesized at various CO/Ar ratios (duplication # 2 )

(a:0%; b: 25%; c:50%; d:75% ; e:100%).



**Fig. S3** TEM images of Pt/C NPs synthesized in PVP concentrations of (a) 1 and (b) 2 M.

**Fig. S4** represents the typical powder X-ray diffraction (XRD) patterns obtained for the homemade Pt/C catalysts. The broad peak located at  $\sim 24^\circ$  in all patterns originates from the (0002) hexagonal phase of Vulcan XC-72 carbon. The other four peaks are the characteristic peaks of the face center cubic (FCC) crystalline structure of platinum corresponding to the planes (111), (200), (220), and (311) at  $2\theta$  of ca.  $40^\circ$ ,  $48^\circ$ ,  $70^\circ$  and  $84^\circ$ , respectively. XRD patterns reveal that the homemade catalysts are of single phase solid solution. The average grain sizes of all the catalysts were calculated by employing the Scherrer equation.<sup>36</sup> The calculated grain sizes are fairly consistent with the particle diameters estimated from the HR-TEM images shown in the XRD patterns, as listed in Table 1.

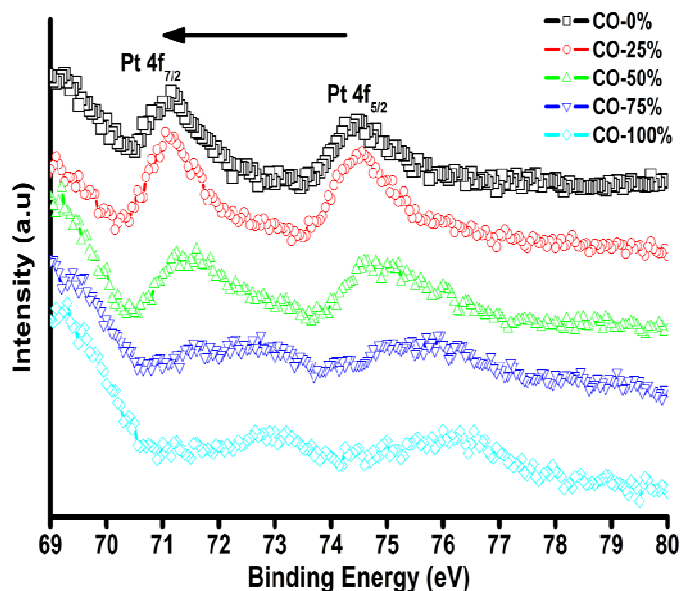


**Fig. S4** XRD patterns of the synthesized Pt/C samples for different duplications.

We used X-ray photoelectron spectroscopy (XPS) to probe the chemical state of the synthesized Pt/C samples. The shape and position of the BE are characteristic of a probed element undergoing specific chemical bonding. **Fig. S5** shows representative XPS spectrum of the Pt 4f region, which reveals the presence of a main band corresponding to  $4f_{5/2}$  photoelectrons, accompanied by one associated with  $4f_{7/2}$  photoelectrons, with a gap of 3.3 eV. Interestingly, binding energies for the observed Pt  $4f_{7/2}$  and  $4f_{5/2}$  bands of the synthesized Pt/C NPs displays a shift to higher energies with an increase in the CO/Ar ratio in comparison with



those of Pt foil ( $\text{Pt}^0$ ). This finding implies that the positions of the observed  $\text{Pt } 4f_{7/2}$  and  $4f_{5/2}$  bands of the synthesized Pt/C NPs possess a size-dependent property, mainly attributable to size-induced changes in the initial-state band structure and the final-state relaxation.



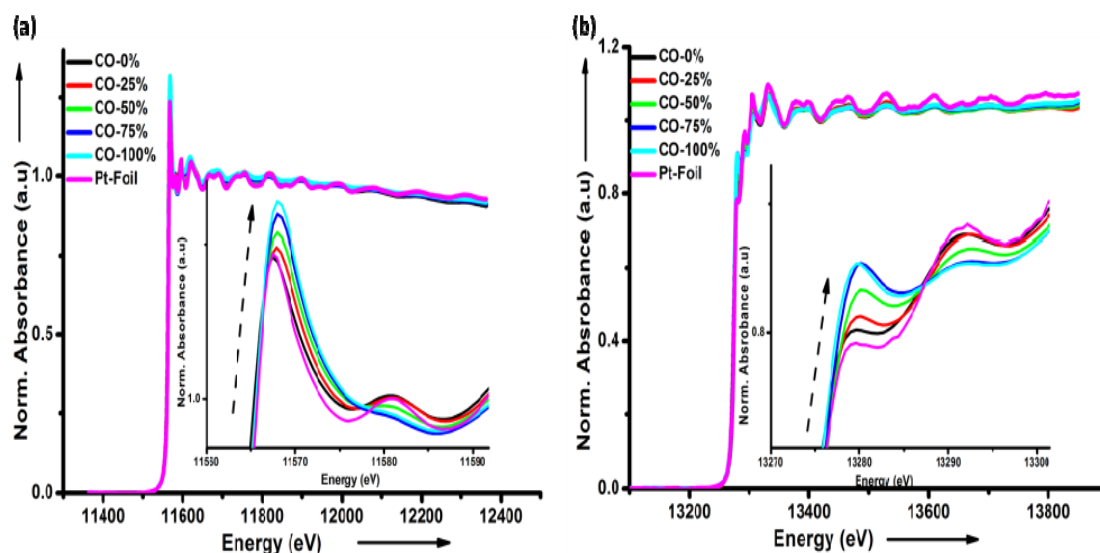
**Fig. S5** XPS Pt-4f spectra of the size-dependent Pt/C sample ; the solid arrow indicates the shift to lower binding energy upon increasing particle size.

#### Evaluation of the number of unfilled states ( $h_{Ts}$ )

The X-ray absorption near-edge structure (XANES) provides a fingerprint of the electronic state and site symmetry of the absorbing element. The intensity of the sharp peaks at the Pt- $L_{III}$  and Pt- $L_{II}$  edges (insets in **Fig. S6a** and **S6b**, respectively), referred to as the “white line,” is primarily dependent on the excitation of the transition matrix elements from  $2p_{3/2}$  to  $5d$ ; it is also very sensitive to the presence of unfilled state of  $d$  electron.

Dashed arrows in **Fig. S6a** and **Fig. S6b** indicate the increases in the white line intensities upon decreasing the cluster size. The white line intensities at both edges increased upon increasing the CO/Ar ratio. We interpret the increased intensity simply to an increase in the level of unfilled  $d$  states. In accordance with the results of our XANES, EXAFS, and TEM

analyses, we demonstrate that the unfilled  $d$  states of Pt possesses a strong size-dependence property. To quantify the differences in unfilled  $d$  states between the Pt nanoparticles and a reference Pt foil, we compared the fractional change in the total number of unfilled  $d$  states ( $h_{TS}$ ) of the sample with that of the reference foil ( Table S1 and **Fig. 3**).<sup>SI-4-8</sup>



**Fig. S6** XANES analyses of the synthesized Pt/C samples prepared at various CO/Ar ratios and of a reference foil. XANES at the (a) Pt-L<sub>III</sub> and (b) Pt-L<sub>II</sub> edges.

A method modified by Reifsnnyder et al., which was originally developed by Mansour et al., was employed in this study to quantify the unfilled  $d$  states of the synthesized Pt/C catalysts<sup>SI-4-5</sup>. After subtracting the background of the Pt foil data from the catalyst data, the resulting curves were numerically integrated between  $-10$  and  $+14$  eV relative to the Pt absorption edge for both the L<sub>II</sub> ( $\Delta A_2$ ) and L<sub>III</sub> ( $\Delta A_3$ ) edges. The fractional change in the total number of unfilled Pt  $d$  band states compared with that of the reference Pt foil ( $f_d$ ) was estimated using equation (1). All the areas ( $A_{3s}$ ,  $A_{2s}$ ,  $A_{3r}$ , and  $A_{2r}$ ) were normalized by multiplying by the X-ray absorption cross section ( $\sigma$ ) at the respective edge jumps. The values of  $\Delta A_i$  ( $i = 2$  or  $3$ ) were defined as the differences in normalized areas between the samples and the reference foil. Because the number of unfilled  $d$  states in the reference material ( $h_{Tr}$ ) is

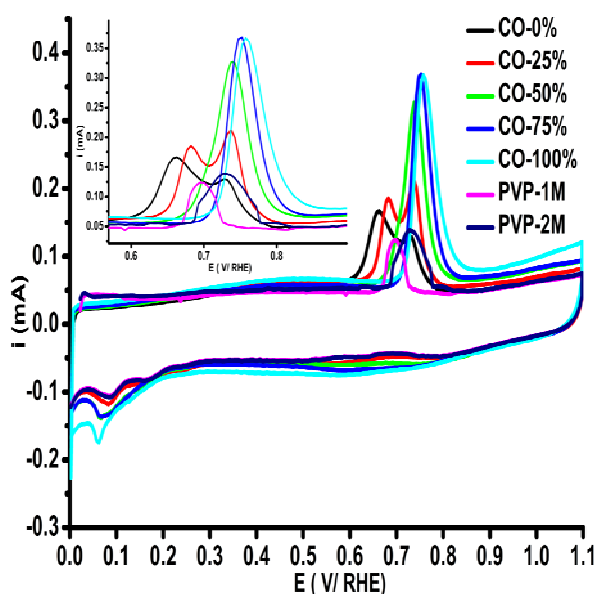
known (equal to 1.60), the number of unfilled  $d$  states in the sample ( $h_{Ts}$ ) was calculated using eq. (2); the corresponding values are listed in Table S1.

$$f_d = \frac{\sigma_3 \Delta A_3 + (1.11 \sigma_2 \Delta A_2)}{\sigma_3 A_{3r} + (1.11 \sigma_2 A_{2r})} \quad (1)$$

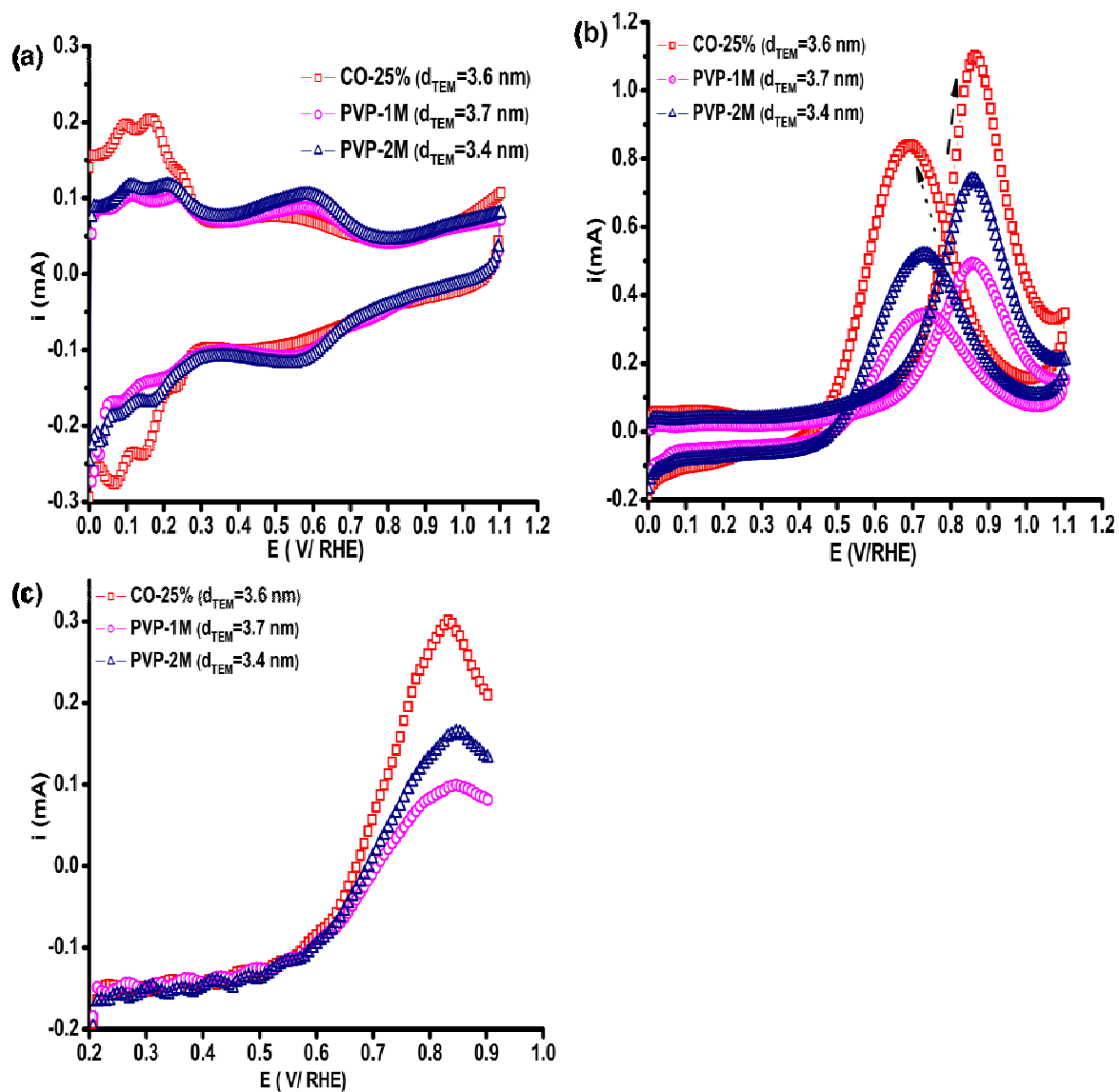
$$h_{Ts} = (1 + f_d) h_{Tr} \quad (2)$$

Table S1. Fractional changes in the unfilled  $d$  states ( $f_d$ ) and the number of unfilled states ( $h_{Ts}$ ), determined with respect to those of Pt foil.

Sample	$\Delta A_2$	$\Delta A_3$	$A_{3r}$	$A_{2r}$	$A_{3s}$	$A_{2s}$	$\delta_3$	$\delta_2$	$f_d$	$h_{Ts}$
Pt foil			17.098	11.176	17.098	11.176	1.055	0.493		1.600
CO-0%	0.112	0.433	17.098	11.176	17.532	11.288	2.997	1.383	0.021	1.634
CO-25%	0.341	0.650	17.098	11.176	17.749	11.517	2.122	0.960	0.036	1.658
CO-50%	0.442	0.663	17.098	11.176	17.761	11.618	2.122	0.972	0.039	1.662
CO-75%	0.849	0.573	17.098	11.176	17.671	12.025	2.283	1.045	0.044	1.671
CO-100%	1.066	0.695	17.098	11.176	17.794	12.242	2.024	0.934	0.054	1.687



**Fig. S7** CO stripping voltammograms for the synthesized Pt/C samples in CO-free 0.5 M  $H_2SO_4$ ; scan rate:  $5 \text{ mV s}^{-1}$ .



**Fig. S8** Cyclic voltammograms for the synthesized Pt/C nanoparticles in (a) nitrogen-saturated 0.5 M sulfuric acid, scan rate:  $50 \text{ mVs}^{-1}$ ; (b) nitrogen-saturated 0.5 M methanol-sulfuric acid, scan rate:  $20 \text{ mVs}^{-1}$ ; the dash arrow indicates the forward scan, the dot arrow indicates the backward scan. (c) Linear sweep voltammograms for the synthesized Pt/C nanoparticles in nitrogen-saturated 0.5 M methanol-sulfuric acid scan rate:  $5 \text{ mVs}^{-1}$ , rotating speed: 900 rpm.

**References:**

- [SI-1] H. Song, R. M. Rioux, J. D. Hoefelmeyer, R. Komor, K. Niesz, M. Grass, P. Yang, and G. A. Somorjai, *J. Am. Chem. Soc.*, 2006, **128**, 3027-3037
- [SI-2] Y. L. Hsin, K. C. Hwang, and C. T. Yeh, *J. Am. Chem. Soc.*, 2007, **129**, 9999-10010
- [SI-3] M. Chen, and Y. C. Xing, *Langmuir* 2005, **21**, 9334-9338
- [SI-4] S. N. Reifsnnyder, M. M. Otten, D. E. Sayers, H. H. Lamb, *J. Phys. Chem. B* 1997, **101**, 4972A.
- [SI-5] N. Mansour, J. W. Cook, D. E. Sayers, *J. Phys. Chem.* 1984, **88**, 2330.
- [SI-6] F. J. Lai, W. N. Su, L. S. Sarma, D. G. Liu, C. A. Hsieh, J. F. Lee, B. J. Hwang, *Chem. Eur. J.* 2010, **16**, 4602.
- [SI-7] F. J. Lai, H. L. Chou, L. S. Sarma, D. Y. Wang, Y. C. Lin, J. F. Lee, B. J. Hwang, C. C. Chen, *Nanoscale*, 2010, **2**, 573.
- [SI-8] B. J. Hwang, S. M. S. Kumar, C. H. Chen, R. W. Chang, D. G. Liu, J. F. Lee, *J. Phys. Chem. C* 2008, **112**, 2370.