

## Supporting Information

### **Facile synthesis of high-quality Pt nanostructures with controlled aspect ratio for methanol electro-oxidation**

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## Experimental Section

**Chemicals and Materials.** Platinum(II) acetylacetonate ( $\text{Pt}(\text{acac})_2$ , 97%), polyvinyl pyrrolidone (PVP, MW = 40000), and n-butylamine (99.5%) were purchased from Sigma-Aldrich. Benzyl alcohol (AR), formaldehyde (37% wt. in  $\text{H}_2\text{O}$ ), cyclohexane, and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. Oleylamine (OAm, 80%-90%) was purchased from Aladdin. All the chemicals and materials were used as received.

**Synthesis of Pt Nanobars with different aspect ratios.** Pt nanobars were synthesized by reducing  $\text{Pt}(\text{acac})_2$  with benzyl alcohol in the presence of formaldehyde, OAm and PVP. In a standard synthesis,  $\text{Pt}(\text{acac})_2$  (16 mg), PVP (100 mg), OAm (0.1 mL), formaldehyde (1.5 mL), and benzyl alcohol (10.4 mL) were mixed and stirred for 10 min. The as-prepared homogeneous yellow solution (12 mL) was transferred into a 15 mL of Teflon-lined stainless-steel autoclave and then heated to 180 °C for 15 h. After that, the final product was obtained by centrifugation using a sufficient amount of ethanol, and then re-dispersed in cyclohexane. This process was repeated three times to remove the excess PVP and OAm. Pt nanobars with different aspect ratios were also generated by simply changing the amount of formaldehyde to 0.5, 1 and 2.0 mL.

**Preparation of Carbon-Supported Catalysts.** In a standard preparation, 40 mg of carbon black (Vulcan XC-72) were added into 10 mL of cyclohexane containing 10 mg of Pt nanobars to achieve a Pt mass ratio of 20%. The mixture was sonicated for 10 min and stirred for 24 h. The resultant was precipitated out by centrifugation and re-dispersed in n-butylamine at a concentration of 0.5 mg/mL. The mixture was kept under stirring for 3 days, and then centrifuged and washed three times with methanol.

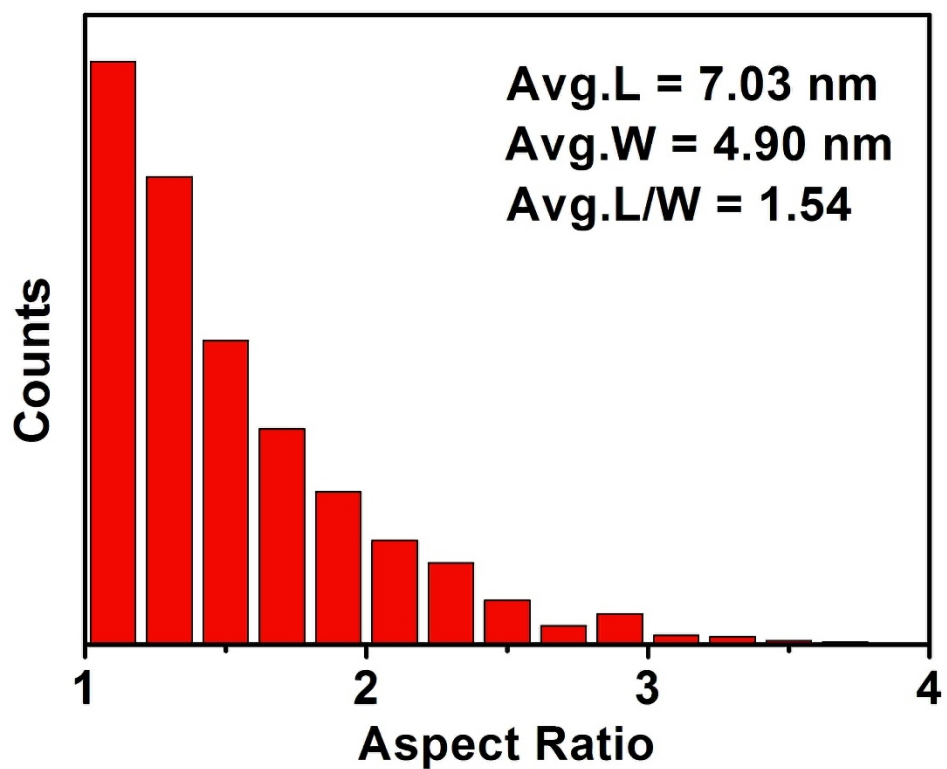
**Morphological, Structural, and Elemental Characterizations.** The samples were characterized by X-ray powder diffraction (XRD) using a Rigaku D/MAX-ga X-ray Diffractometer with graphite monochromatized  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). Transmission electron microscopy (TEM) images were taken using a HITACHI HT-7700 microscope operated at 100 kV. High-resolution transmission electron microscopy (HRTEM) was performed using a FEI Tecnai G2 F20 microscope operated at 200 kV. The concentration of Pt nanocrystals in the solution was determined using inductively coupled plasma atomic emission spectrometry (ICP-AES, IRIS Intrepid II XSP, TJA Co., USA).

**Electrochemical Measurements.** A three-electrode cell was used to measure the electrochemical performances of Pt-based catalysts. The counter electrode was a Pt mesh ( $1 \times 1$

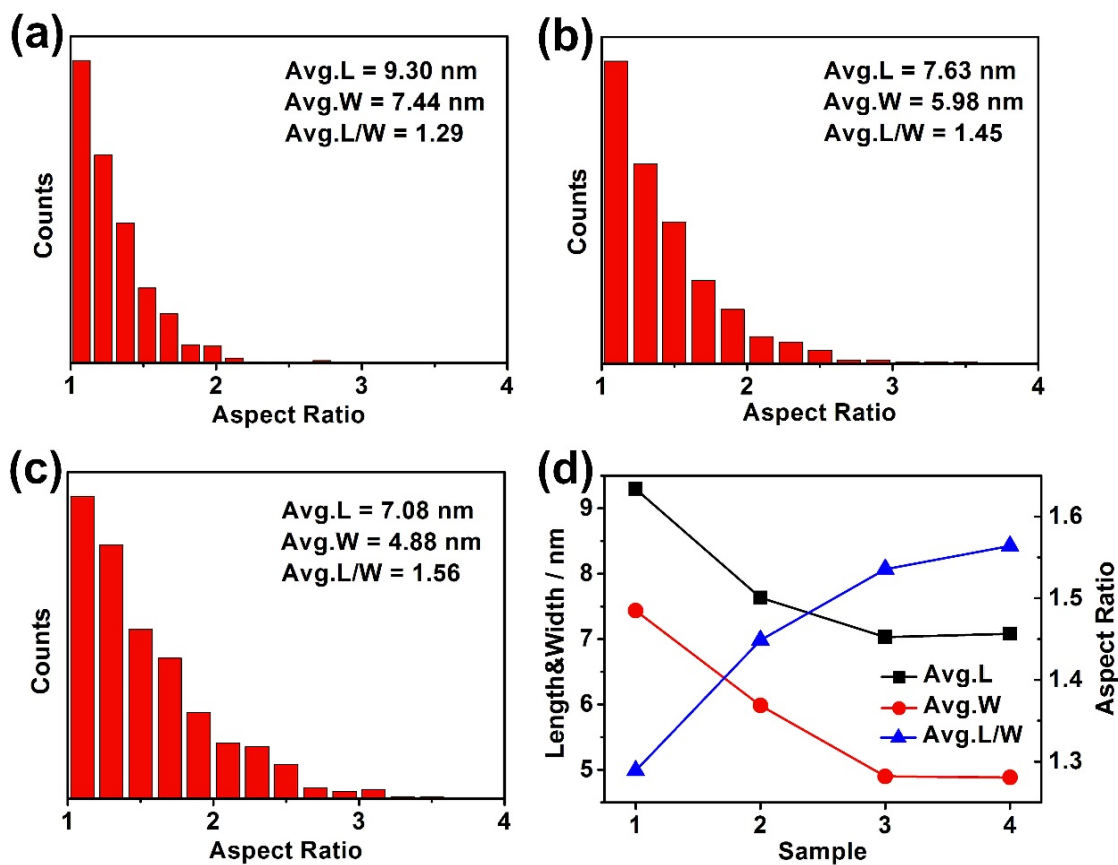
cm<sup>2</sup>) connected to a Pt wire. A HydroFlex hydrogen electrode was used as the reference. To prepare the working electrode, 5 mg of Pt-based catalysts were dispersed in 10 mL of a mixed solvent and sonicated for 10 min. The solvent contained a mixture of de-ionized water, isopropanol, and 5% Nafion 117 solution at the volumetric ratio of 8:2:0.05. After that, 30  $\mu$ L of the catalyst ink was added onto the pre-cleaned glassy carbon electrode and dried in air. For the commercial Pt/C, 20  $\mu$ l of the catalyst ink was used instead. Before electrochemical testing, each electrode was cycled in an Ar-saturated 0.1 M HClO<sub>4</sub> solution for 40 cycles between 0.05 and 1 V at a sweep rate of 50 mV/s. After that, the cyclic voltammetry curves were recorded on the working electrode by cycling between 0.05 and 1.0 V at a sweep rate of 50 mV/s in an Ar-saturated 0.1 M HClO<sub>4</sub> solution. For the electrooxidation of methanol, cyclic voltammograms were recorded in an Ar-purged 0.1 M HClO<sub>4</sub>/0.5 M CH<sub>3</sub>OH solution at a sweep rate of 50 mV/s in the range of 0.05 V to 1.2 V. In CO stripping experiments, the electrodes were pretreated by immersing in a CO-saturated 0.1 mol/L HClO<sub>4</sub> aqueous solution and held at 0.25 V for 20 min before the measurements. The CVs were typically run at the room temperatures using a scan rate of 50 mV/s.

**Table S1.** Mass loading and ECSA of the carbon supported Pt nanobars with different aspect ratios, including commercial Pt/C.

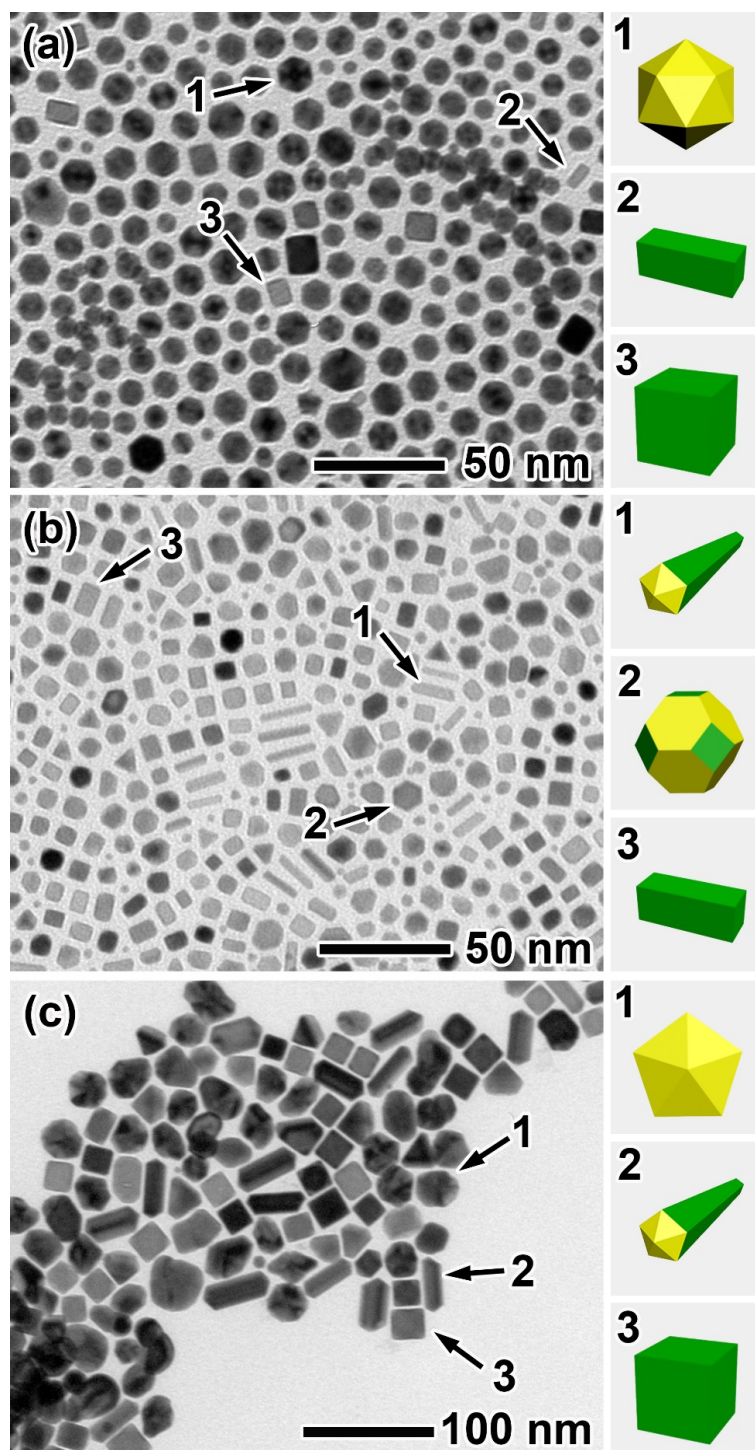
Catalysts	Pt wt% on carbon	Mass loading of Pt ( $\mu\text{g}$ ) in a test	ECSA ( $\text{m}^2/\text{g}_{\text{metal}}$ )
Sample 1 (aspect ratio= 1.29)	14.1%	2.1	21.9
Sample 2 (aspect ratio= 1.45)	16.3%	2.4	30.7
Sample 3 (aspect ratio= 1.54)	14.6%	2.2	27.7
Pt/C (20 wt % 3.2 nm Pt nanoparticles on Vulcan XC-72, E-TEK)	20%	2.0	71.7



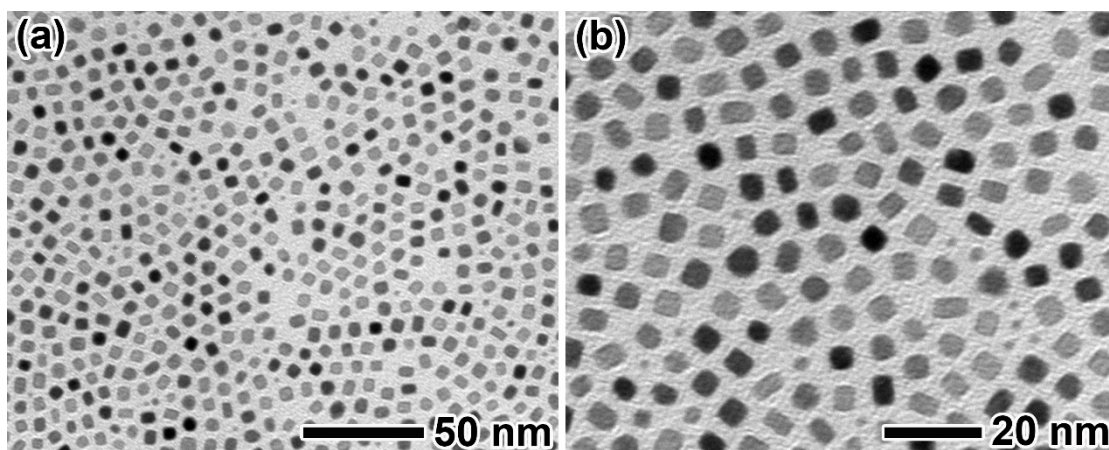
**Fig. S1** Aspect ratio distribution of the Pt nanobars prepared using the standard procedure, together with their average length and width.



**Fig. S2** Aspect ratio distribution of the Pt nanobars prepared using the standard procedure, except for the different amount of formaldehyde: (a) 0.5, (b) 1.0, and (c) 2.0 mL. (d) Plots of average aspect ratio, length, and width of the four afore-mentioned samples, including the one prepared using the standard procedure.

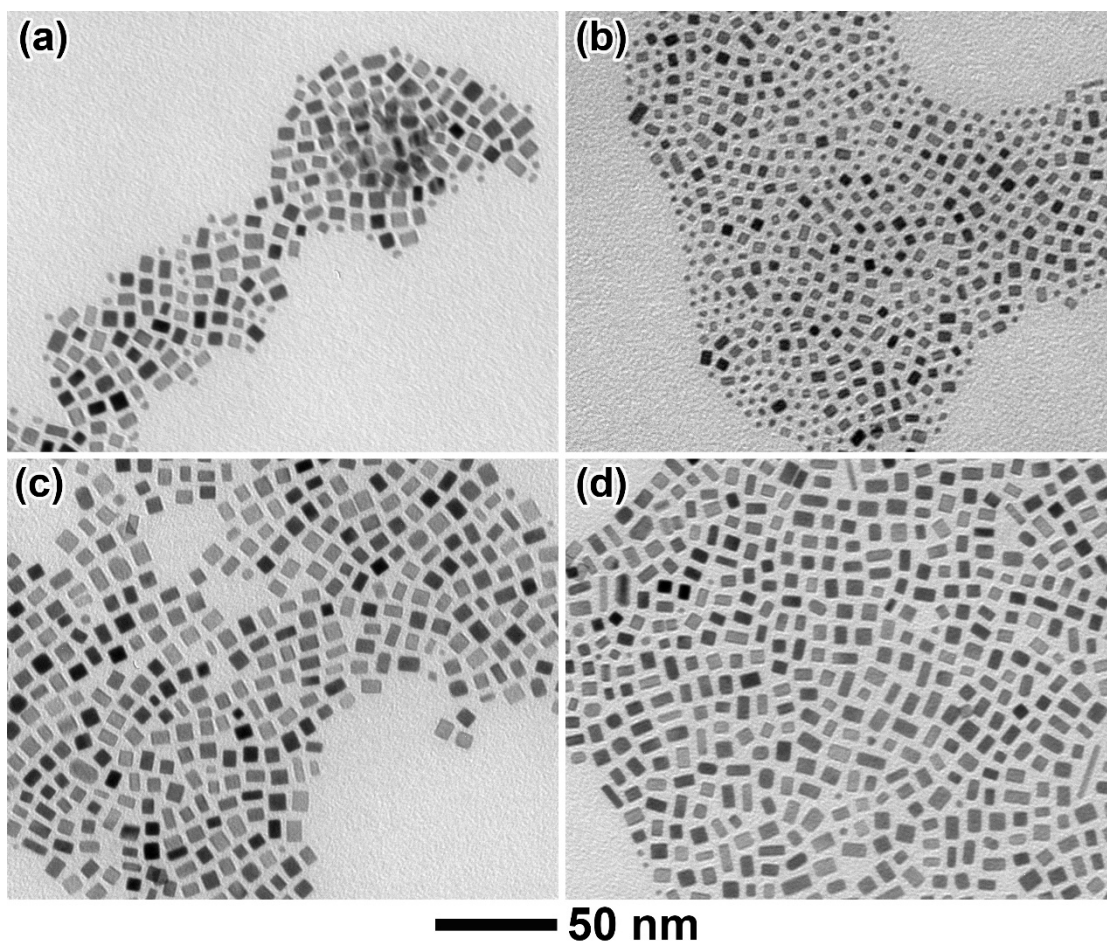


**Fig. S3** TEM images of the Pt nanocrystals prepared using the standard procedure, except for the difference in the amounts of OAm and formaldehyde: (a) in the absence of OAm and formaldehyde, (b) only 0.5 mL formaldehyde, (c) only 0.1 mL OAm.

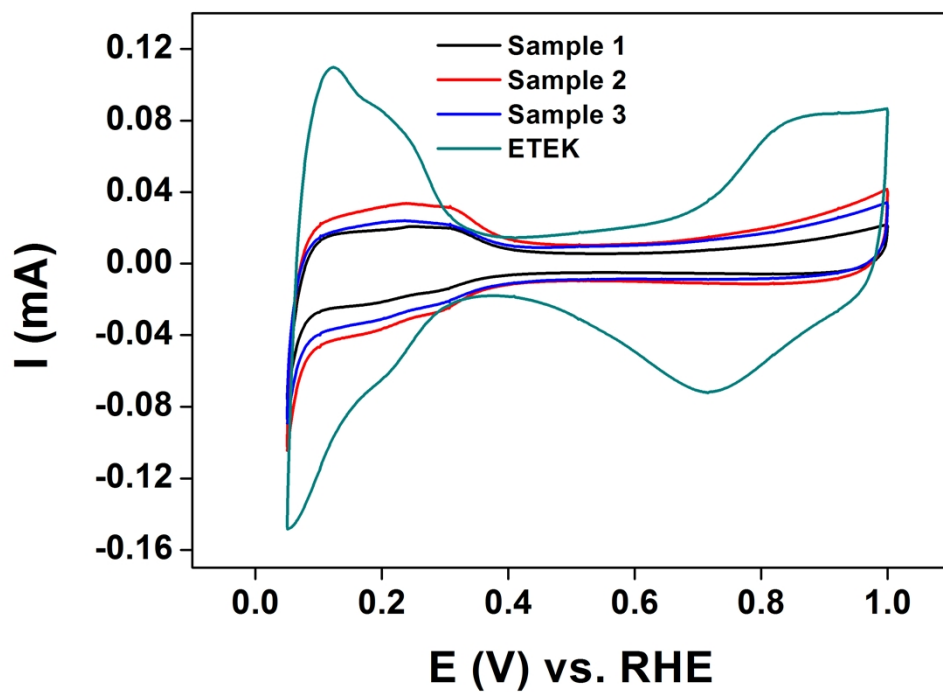


**Fig. S4** TEM images (a, b) of Pt nanobars prepared using the standard procedure, except for replacing formaldehyde with acetaldehyde.

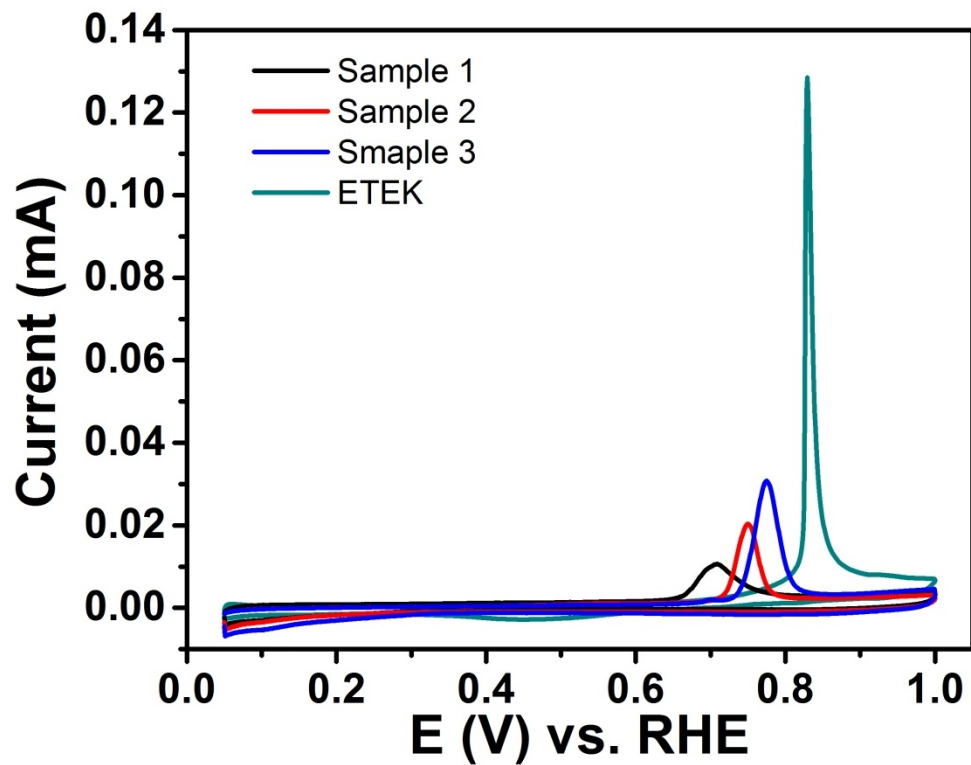




**Fig. S5** TEM images of Pt nanobars prepared using the standard procedure, except for replacing oleylamine with other amines, (a) octylamine, (b) dodecylamine, (c) hexadecylamine, and (d) octadecylamine.



**Fig. S6** Cyclic voltammograms (CVs) of three Pt nanobar-based catalysts (Sample 1 to Sample 3), including commercial Pt/C (ETEK) in a Ar-saturated 0.1 M HClO<sub>4</sub> solution at a sweep rate of 50 mV/s. The CV was recorded after 40-potential cycles with a scan rate of 50 mV/s.



**Fig. S7** CV curves of CO stripping on the surfaces of three Pt nanobar-based catalysts (Sample 1 to Sample 3), including commercial Pt/C (Etek).