

Supporting Information

Rapid and Shape-Controlled Synthesis of “Clean” Star-like and Concave Pd Nanocrystallites and Their High Performance toward Methanol Oxidation

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1. Chemicals and materials

L-ascorbic acid ($C_6H_8O_6$, Beijing Chemical Works, >99.7%), potassium bromide (KBr, Beijing Chemical Works, >99%), sodium hydroxide (NaOH, Beijing Chemical Works, >96%), activated carbon (Vulcan XC-72, Cabot), palladium (II) chloride ($PdCl_2$, Aladdin Reagent, $Pd \geq 60\%$), concentrated hydrochloric acid (HCl, Beijing Chemical Works, 36.5 wt %), methanol (CH_3OH , Beijing Chemical Works, > 99.9%), sulfuric acid (H_2SO_4 , Beijing Chemical Works, 95~98 wt %), commercial carbon supported palladium catalyst (Pd/C, Alfa aesar, 20 wt %), Al_2O_3 powder (Aldrich, 0.5 and 3 μm), and Nafion solution (Sigma-Aldrich, 5 wt %) were used as received. Ultrapure water with the specific resistance of 18.2 $\mu S/cm$ was obtained by reversed osmosis followed by ion-exchange and filtration. Glassy carbon electrode (GC, 5 mm in diameter) was purchased from Tianjin AidaHengsheng Tech. Co, China.

2. Preparation of Pd NSs

A H_2PdCl_4 solution (34.46 mM) was prepared at 363 K by dissolving 0.76 g of PdCl_2 in 15 ml of hydrochloric acid (37 wt %) under vigorously stirring, then diluted with 85 mL ultrapure water. In a typical synthesis, 1 mL of H_2PdCl_4 solution (34.46 mM) and 3 mg of KBr were added into 100 mL of ultrapure water (pH = 2.18), followed by adding L-Ascorbic acid (3.3 mL, 57 mM) with vigorous shaking, and then left undisturbed for 5 minutes. Then, the gray suspension was obtained. While different control experiments were performed, the total volume of the solution maintains 104.3 mL. The synthesis of Pd (in-situ)/XC-72 is same with Pd NSs, only 14.7 mg of XC-72 carbon was dispersed in 100 mL ultrapure water before H_2PdCl_4 was added.

3. Preparation of Pd CNs

The synthesis of Pd CNs is the same with Pd NSs except adding NaOH (0.66 mL, 1.25 M) before adding L-ascorbic acid into solution (pH = 3.16).

4. Preparation of the thin-film working electrode

14.7 mg XC-72 carbon dispersed in 20 mL of water was added into the as-prepared brown suspension. After durative sonication and agitation for 12 h, Pd NCs/XC-72 (20 wt %) was collected by consecutive washing/centrifugation cycles for three times with water. Then the Pd NCs/XC-72 was dispersed in 30 mL ethanol again, and after durative sonication and agitation for another 12 h, Pd NCs/XC-72 was collected by centrifugation. The collected product was then dried at 60 °C for 12 h.

The GC electrode was sequentially polished with 3 and 0.5 μm Al_2O_3 paste (mixed with Al_2O_3 powder and ultrapure water). After the mechanical pretreatment, the electrode was cleaned by sonication in ultrapure water. To prepare the working electrode, 5 mg of the catalysts was

dispersed in diluted Nafion alcohol solution which contained 1000 μL ethanol and 50 μL Nafion (5 wt %), and was sonicated for 1 h to obtain a uniform suspension. Next, 10 μL of the suspension was pipetted onto the flat glassy carbon electrode. The coated electrode was then dried at room temperature for 10 min.

5. Catalyst characterization

5.1 Powder X-ray diffraction (XRD)

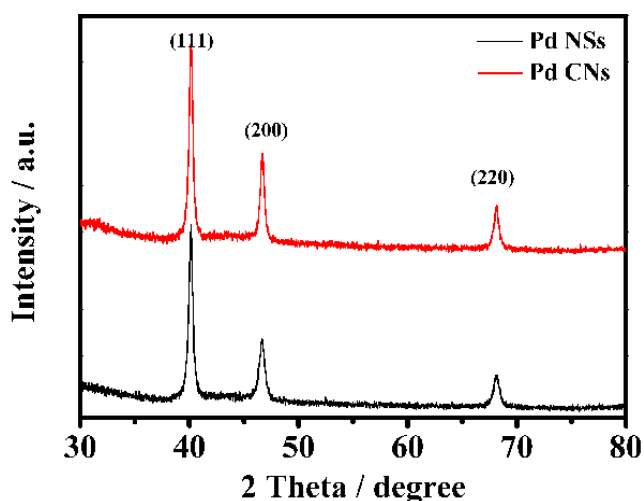


Figure S1. XRD profile of the as-prepared Pd NSs and Pd CNs.

XRD measurements were performed on a Rigaku-Dmax 2500 diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15405 \text{ nm}$) from 30 to 80 degree at a scanning rate of 5 degree per minute. The samples were grinded and flattened in a piece of glass with a hole.

5.2 Scanning electron microscopy (SEM) and transmission electron microscope (TEM)

The morphology and dimensions of as-prepared samples were obtained using a field emission scanning electron microscopy instrument (Hitachi S-4800), operating at an accelerating voltage of 10 kV. Specimens for SEM were prepared by dispersing as-prepared product in

ethanol by sonicating for about 10 min, and then depositing the suspension onto a piece of ITO glass, attached to a SEM brass stub.

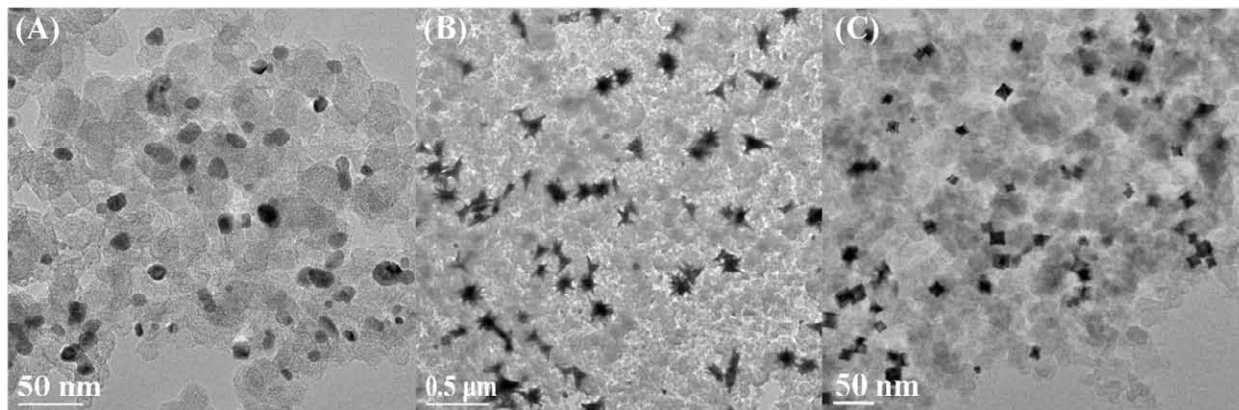


Figure S2. TEM images of (A) Pd (in-situ), (B) NSs, (C) CNs supported on XC-72.

From Figure S2B and S2C, although Pd NPs cannot be loaded on XC-72 uniformly, yet no visible aggregation can be found.

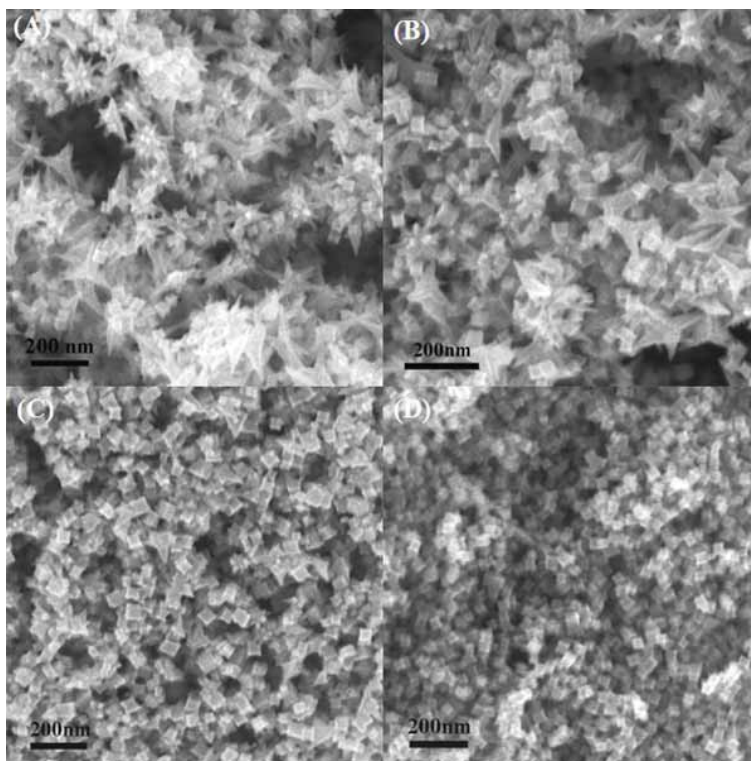


Figure S3. SEM images of Pd NCs prepared by using the typical procedure, except adding the different quantity of NaOH (1.25 M): (A) 0.5 mL, (B) 0.7 mL, (C) 0.9 mL, (D) 1.1 mL.

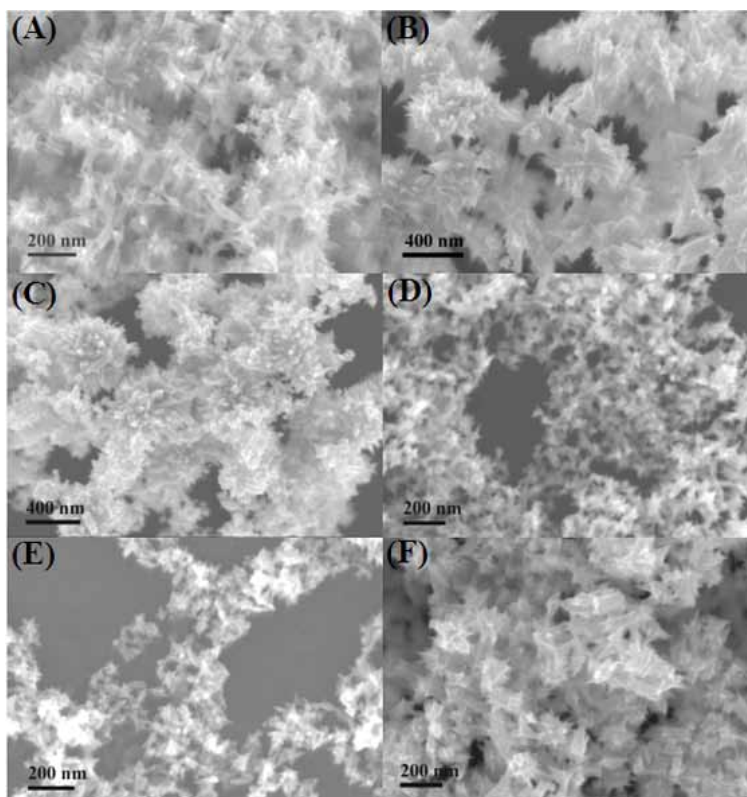


Figure S4. SEM images of Pd NCs prepared by using the typical procedure, except different concentration of: (A) 0.03 mM and (B) 3 mM KBr, (C) 0.4 mM and (D) 10 mM AA, (E) 0.068 mM and (F) 1.7 mM H₂PdCl₄ (The pH value was tune to 2.18 by HCl or NaOH.).

Low- to high-resolution transmission electron microscopies were performed using a FEI Tecnai G2 S-Twin instrument with a field emission gun operating at 200 kV, and images were acquired digitally on a Gatan multipole CCD camera. Specimens for TEM in Fig. 2 were prepared by dispersing the samples in ethanol, sonicating for 20 min to ensure adequate dispersion, and evaporating one drop of the suspension onto a 300 mesh Cu grid, coated with a lacey carbon film.

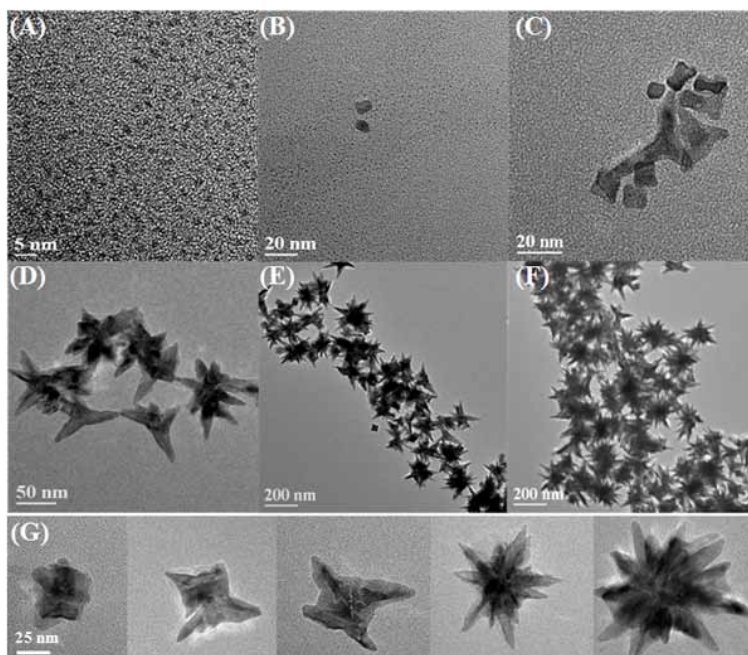


Figure S5. TEM images showing the course of morphological evolution for Pd NSs. The reaction time was (A) 1, (B) 2, (C) 3, (D) 4 min, (E) 5 min, and (F) 10 min, respectively. (G) Evolution process from Pd seeds to Pd NSs.

5.3 Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectra were obtained with BRUKER Vertex 70 FT-IR spectrometer.

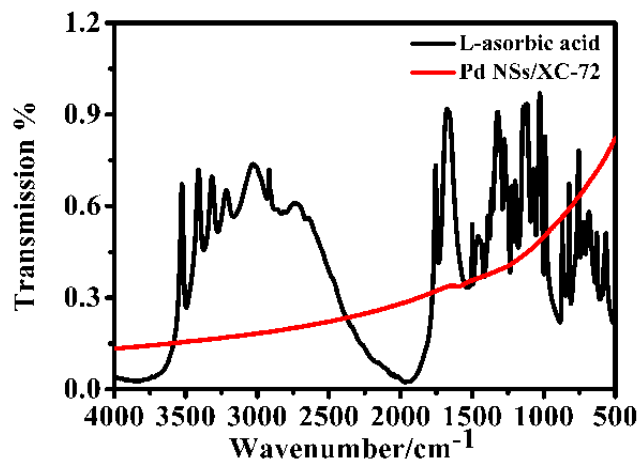


Figure S6. FT-IR spectra of L-ascorbic acid and the Pd NSs after washing.

5.4 X-ray photoelectron spectrometer (XPS)

XPS spectra were obtained with an ESCALABMKLL X-ray photoelectron spectrometer using an Al K α source.

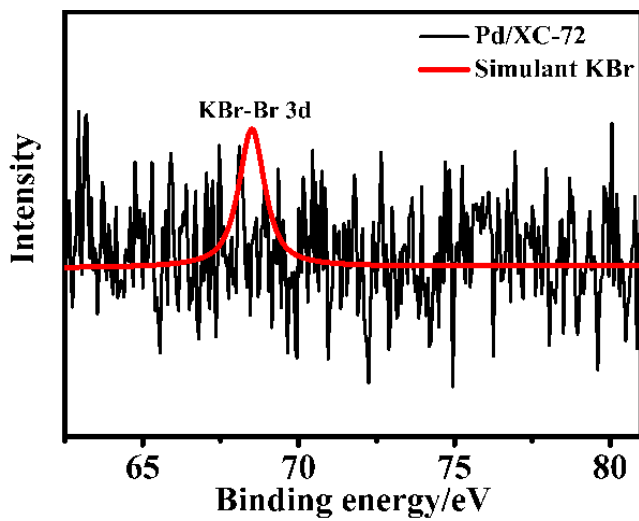


Figure S7. XPS spectra of the Pd NSs after washing.

5.5 Electrochemical characterization

Electrochemical experiments were carried out in a standard three-electrode cell at room temperature (about 298 K). The working electrode was the thin-film electrode with catalysts. Pt foil and Ag/AgCl were used as the counter and reference electrodes, respectively. All potentials in this report referred to Ag/AgCl. All electrolyte solutions were deaerated with high-purity nitrogen for at least 20 min prior to any measurement. Electrode potential was controlled by an EG&G (model 273) potentiostat/galvanostat system.

5.5.1 Electrochemical active surface (EAS)

CO stripping voltammetry (CO_{sv}) was employed to evaluate the electrochemically active surface area of the catalysts as well as their anti-poison ability. The 0.5 M H_2SO_4 solution was first bubbled with a pure N_2 for 30 min in order to remove the dissolved oxygen. CO was then purged into solution for 30 min to allow complete adsorption of CO onto the electrocatalyst, while maintaining a constant potential at 0 V. Excess CO was then purged with N_2 for 40 min. The amount of CO_{ads} was evaluated by integrating the CO_{ads} stripping peak (electrode potential scan rate: 50 mV/s), corrected for electric double-layer capacitance. The specific surface area of Pd was estimated using two assumptions: (1) there was a monolayer of linearly adsorbed CO and (2) the coulombic charge required for oxidation was $420 \mu\text{C}/\text{cm}^2$.

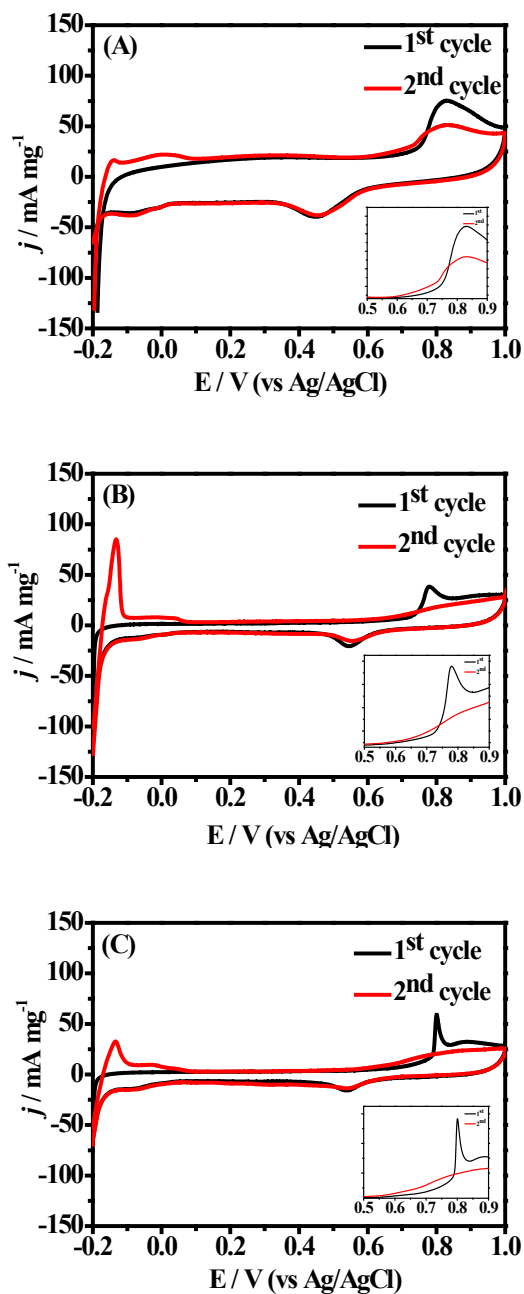


Figure S8. CO stripping voltammograms on Pd-based catalysts in 0.5 M H_2SO_4 solution at a scan rate of 50 mV/s: (A) commercial Pd/C, (B) Pd NSs/XC-72, (C) Pd CNs/XC-72. Inset: amplificatory CO_{sv} from 0.5 V to 0.9 V.

EAS (m^2/g): commercial Pd/C, 80.5; Pd NSs/XC-72, 43.7; Pd CNs/XC-72, 40.9.

5.5.2 Catalyst stability

The cycle stability tests of the samples were done at the same condition as the catalytic activity at a scan rate of 50 mV/s.

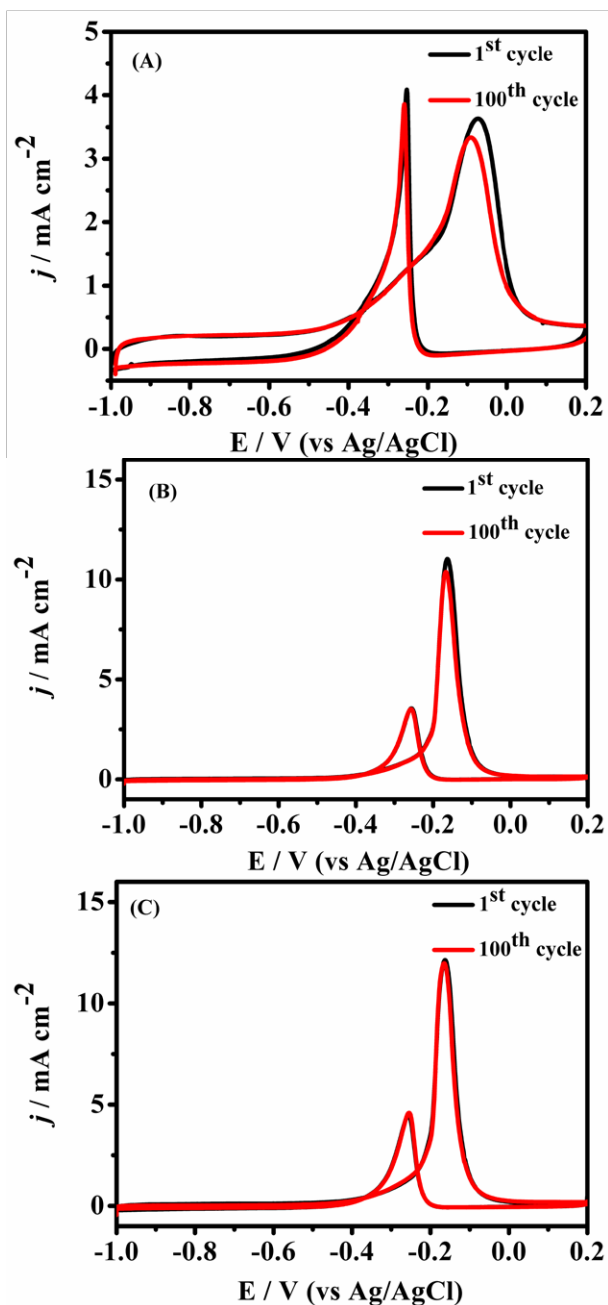


Figure S9. Electrocatalytic stability tests of Pd-based catalysts at a scan rate of 50 mV/s in 0.5 M NaOH with 1 M CH_3OH at room temperature: (A) commercial Pd/C, (B) Pd CNs/XC-72, and (C) Pd NSs/XC-72.

Chronoamperometric curves were obtained in 0.5 M NaOH solution containing 1 M CH₃OH at the potential of -0.23 V for 1800 s.

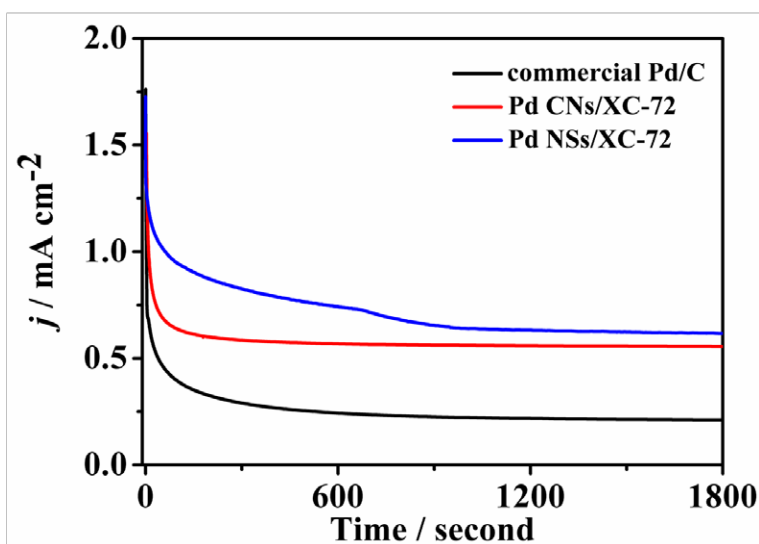


Figure S10. Chronoamperometric curves in deaerated 0.5 M NaOH solution containing 1 M CH₃OH at the potential of -0.23 V for 1800 s at room temperature.