Spiny-porous platinum nanotubes with enhanced
electrocatalytic activity for methanol oxidation

Yunpeng Zuo, Kai Cai, Long Wu, Tingting Li, Zhicheng Lv, Jiawei Liu, Kang Shao and Heyou Han*

State Key Laboratory of Agricultural Microbiology, College of Science,
Huazhong Agricultural University, Wuhan 430070, China.

* To whom correspondence should be addressed. Tel: +86-27-87282043; fax: +86-27-87282043.

E-mail: hyhan@mail.hzau.edu.cn
Experimental Details

Chemicals: Hexadecyltrimethylammonium bromide (CTAB, 99%), sodium dodecyl sulfate (SDS, 99%), Pt/C (20% Pt) were purchased from Sigma-Aldrich. Tellurium dioxide powder (TeO₂, 99.99%) was purchased from Aladdin Chemistry Co., Ltd. Hydrazine monohydrate (85%, AR), chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O, AR), and sodium hydrate (NaOH, AR) were supplied by Sinopharm Chemical Reagent Co., Ltd. Unless special instructions, other chemicals were of analytical reagent. Ultrapure water for the whole experiment process was with a conductivity of 18.25 MΩ-cm.

Apparatus: The energy-dispersive X-ray spectroscopy (EDS) analysis was also done using a JEM-2010FEF transmission electron microscope with an EDAX attachment operating at an accelerating voltage of 200 kV. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) measurements were made on a JEM-2010FEF high-resolution transmission electron microscopy at an accelerating voltage of 200 kV. The compositions of Pt nanomaterials were determined by ICP–AES (ELAN 6000, Perkin-Elmer). The X-ray diffraction (XRD) analysis was carried out on a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation. Ultraviolet-Visible (UV-Vis) absorption spectra were recorded on Nicolet Evolution 300 Ultraviolet-Visible spectrometer.

Preparation of Te nanowires (TeNWs): TeNWs were prepared according to the method reported previous¹,², However, the original method was improved. 10 mL N₂H₄·H₂O was slowly added into a reaction bottle with TeO₂ powder (30 mg) at 30°C under constant magnetic stirring. With the reaction continuous, the color of the solution gradually changed, and then the solution changed color to blue after 30 mins, the special TeNWs obtained, However, to obtain well-defined TeNWs, the mixture should dilute 10-fold with SDS (10 mM) to stabilize the as-prepared TeNWs and the products subjected to a centrifugation/wash cycle to remove most of the matrices, including SDS and hydrazine. Finally as-prepared TeNWs dispersed in 9 ml of water.

Synthesis of spiny-porous Pt nanotubes (SP-PtNTs): In a typical synthesis, 1ml as-prepared TeNWs which subjected to centrifugation/wash one time were dispersed in 6 mL of CTAB solution (30 mM) under constant magnetic stirring, after 10 mins, 650 ul H₂PtCl₆ (~1 mmol) that the pH was adjusted to 7.0 with 0.1 M NaOH was slowly added to the mixture, 30 mins later, the solution changed color from blue to amber and the SP-PtNTs were obtained after a centrifugation/wash cycle to remove most of the matrices, then the products, that was redispersed in water (1 mL) and after a centrifugation/wash cycle, SP-PtNTs were obtained.
**Synthesis of porous Pt nanotubes (P-PtNTs):** In this process of synthesis, 1ml as-prepared TeNWs which subjected to a centrifugation/wash cycle were dispersed in 6 mL of CTAB solution (12 mM) at under constant magnetic stirring, after 20 mins, 350 ul H₂PtCl₆ (~1 mmol, PH=7) was slowly added to the mixture until the concentration of the chloroplatinic acid up, 25 mins later, the solution changed color from blue to amber and the P-PtNTs were obtained after a centrifugation/wash cycle to remove most of the matrices, then the products processed according to the above method just as the synthesis of SP-PtNTs.

**Electrocatalytic experiment:** In order to clean the surface coating, GCE (3 mm in diameter) was polished with 1.0 and 0.3 μm alumina slurry sequentially and then washed ultrasonically in water and ethanol for a few minutes. For methanol oxidation, a total of 5 μL of SP-PtNTs (0.6 mg/mL), P-PtNTs (1.2 mg/mL) and commercial Pt/C catalyst (5 mg/mL and the content of Pt is 20 wt.% ) was dropped on the pretreated GCE surface dried at room temperature and then 5 μL of 0.5 wt% nafion solution dissolved in ethanol was dropped on the modificatory GCE surface and dried at room temperature before electrochemical experiments.²

![Fig. S1](image.png) a) TEM images of TeNWs. b) UV-vis absorption spectra of TeNWs.
**Fig. S2** XRD pattern of the SP-PtNTs.

**Fig. S3** EDS spectrum of the SP-PtNTs.
**Fig. S4**  TEM images of the Pt materials with different amounts of CTAB; a) without CTAB; b) 0.0350g CTAB; c) 0.0650g CTAB.

References

