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Ternary Pt/Ru/SnO_2 hybrid architectures: unique carbon-mediated 1-D configuration and their electrocatalytic activity to methanol oxidation

Siyuan Yang,[a] Chen Zhao,[b] Chunyu Ge,[a] Xianming Dong,[a] Xiaotang Liu,[a] Yingju Liu,[a] Yueping Fang,*[a] Hongqiang Wang[b] and Zesheng Li*[b]

[a] *Institute of Biomaterial, College of Science, South China Agricultural University, Guangzhou 510642, China;*
[b] *Key Laboratory for the Chemistry and Molecular Engineering of Medicinal Resources (Ministry of Education of China), School of Chemistry & Chemical Engineering of Guangxi Normal University, Guilin 541004, China*
Corresponence author: Yueping Fang Tel: 86-20-85285565. Fax: 86-20-85285565. E-mail: ypfang@scau.edu.cn; Zesheng Li E-mail: lzs212@163.com.

Experimental section

Synthesis of Pt/Ru/SnO_2 hybrid samples

For the synthesis, SnO_2@C core-shell nanochains-built 3-D superstructures (SnO_2@C precursor) were first synthesized in high yield by an easy combined hydrothermal/sintering strategy reported previously by our group.[S1] Afterwards, PtRu nanoparticles were synthesized in situ on the carbon surface of SnO_2@C nanochains through a controllable glycol reduction approach in a facile component-to-temperature regulated system. By governing the ratio of glycol/water composition, various azeotropy points were readily achieved to reach the tunable reaction temperature of the system (see Fig. S1 for details).

Typically, to deposit the PtRu nanoparticles on the on the carbon layer of the SnO_2@C precursor (30 wt.% metal content, atomic ratio of Pt:Ru = 2:1), the SnO_2@C precursor were placed in a 50mL flask, to which 30.0mL of ethylene glycol/water mixed solution (alterable volume ratio) was added. An appropriate amount of stock solutions of the H_2PtCl_4 and $RuCl_3$ was added. The reduction reactions were performed under reflux conditions for 2 h with continuous magnetic stirring. In this case, 40%, 60% and 80%, three volume ratio of glycol were selected, corresponding to samples of Pt/Ru/SnO_2 (2.6 nm PtRu NPs), Pt/Ru/SnO_2 (3.2 nm PtRu NPs) and Pt/Ru/SnO_2 (4.3 nm PtRu NPs), respectively. For comparison, Pt/SnO_2 sample was also prepared without using $RuCl_3$.

Characterization of materials

The structure and morphology of the as-prepared samples were analyzed by X-ray diffraction (Rigaku, D/max 2500v/pc), field emission scanning electron microscopy (Philips, FEI Quanta 200 FEG), and transmission electron microscopy (JEOL-2010 microscope operated at 200 kV). The chemical valence of metals in catalyst was analyzed by X-ray photoelectron spectroscopy (Krato Axis Ultra DLD) using Al Kα radiation (1486.71 eV). At the same time, Pt and Ru mass percent of all the catalysts samples were determined by using inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis.

Electrochemical measurement

As a typical process, 5 mg as-prepared catalyst samples were dispersed in 1.95 mL ethanol and a 0.5 mL 0.5 wt% Nafion suspension under ultrasonic agitation to form the electrocatalytic ink. For the methanol oxidation reaction, the catalyst ink was deposited on the surface of the glassy carbon rod and dried at room temperature. The electrochemical measurements were performed in a three-electrode cell on a potentiostat (IM6e, Zahner-Electrik, Germany) at 25 ^oC controlled by a water-bath thermostat. A platinum foil and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively.

[s1] (a) B. Zhang, X. Yu, C. Ge, X. Dong, Y. Fang, Z. Li and H. Wang, *Chem. Commun.*, 2010, **46**, 9188. (b) X. Yu, S. Yang, B. Zhang, D. Shao, X. Dong, Y. Fang, Z. Li and H. Wang, *J. Mater. Chem.*, 2011, **21**, 12295.

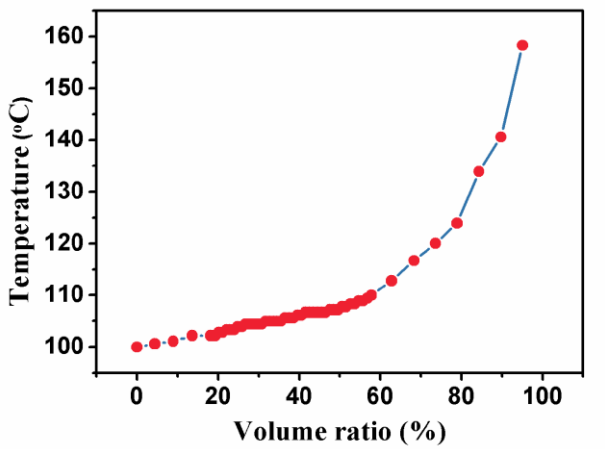

Fig. S1 Azeotropy points of glycol/water mixture as a function of glycol volume ratio.

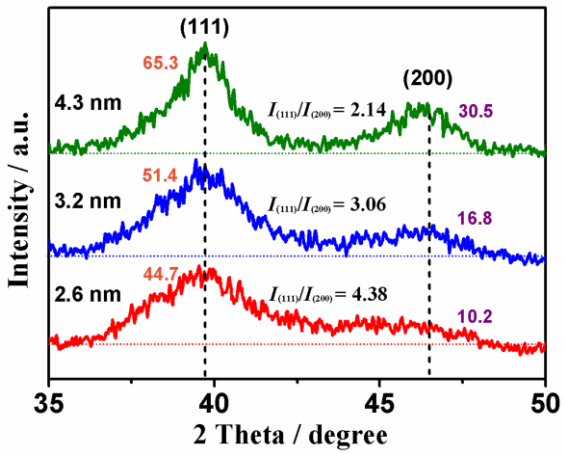

Fig. S2 Intensity ratio of (111) to (200) diffractions of PtRu nanoparticles with various sizes. The $I_{(111)}/I_{(200)}$ ratio of PtRu nanoparticles increases with the decrease of their sizes.

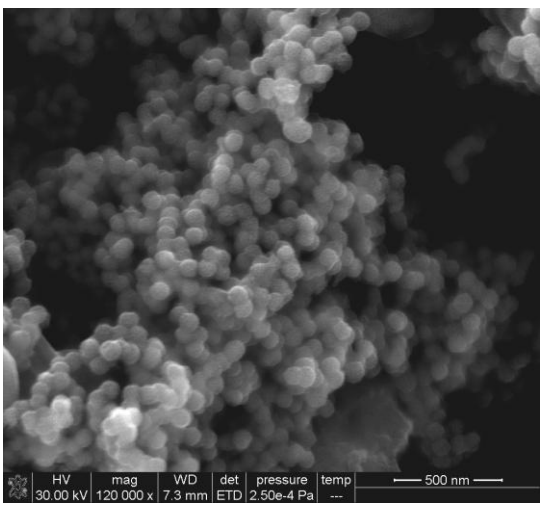

Fig. S3 Typical 3-D network architecture of the Pt/Ru/SnO_2 hybrid sample.

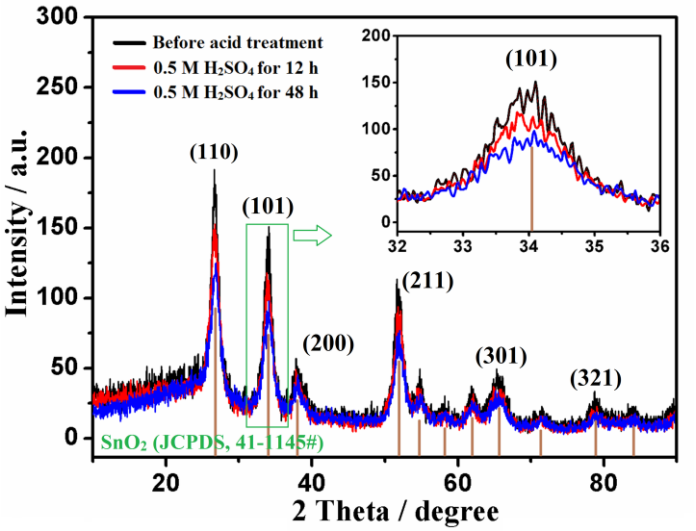

Fig. S4 XRD patterns of the SnO_2@C core-shell nanochains: before acid treatment (black) and after 0.5 M H_2SO_4 treatment for 12h (red) and 48h (blue).