



UNIVERSITY
OF WOLLONGONG
AUSTRALIA

University of Wollongong
Research Online

Australian Institute for Innovative Materials - Papers

Australian Institute for Innovative Materials

2017

Platinum-Cobalt Bimetallic Nanoparticles with Pt Skin for Electro-Oxidation of Ethanol

Binwei Zhang

University of Wollongong, Xiamen University, bz370@uowmail.edu.au

Tian Sheng

Xiamen University

Yunxiao Wang

University of Wollongong, yunxiao@uow.edu.au

Xi-Ming Qu

Xiamen University

Jun-Ming Zhang

Xiamen University

See next page for additional authors

Publication Details

Zhang, B., Sheng, T., Wang, Y., Qu, X., Zhang, J., Zhang, Z., Liao, H., Zhu, F., Dou, S., Jiang, Y. & Sun, S. (2017). Platinum-Cobalt Bimetallic Nanoparticles with Pt Skin for Electro-Oxidation of Ethanol. *ACS Catalysis*, 7 (1), 892-895.

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au

Platinum-Cobalt Bimetallic Nanoparticles with Pt Skin for Electro-Oxidation of Ethanol

Abstract

In order to maximize the Pt utilization in catalysts and improve catalytic processes, we report a convenient strategy for preparation of Pt₃Co with Pt-skin structured bimetallic nanocatalysts directly supported on porous graphitic carbon. Notably, the thickness of the Pt-skin is only 1-2 atomic layers, about 0.5 nm. Surprisingly, the bimetallic nanocatalysts composed of Pt₃Co with Pt-skin are first used as ethanol electro-catalysts, with the mass activity of 0.79 mA/gPt-1, which is a 250% enhancement compared with commercial Pt/C (0.32 mA/gPt-1). On the basis of the results of electrochemical in situ Fourier transform infrared spectroscopy (FTIRS) and density functional theory (DFT), a new ethanol electro-oxidation enhancement mechanism is proposed in which Pt₃Co with Pt-skin promotes partial oxidation of ethanol over C-C bond cleavage, thereby resulting in higher CH₃COOH production than CO₂ production.

Keywords

ethanol, bimetallic, electro-oxidation, nanoparticles, skin, pt, platinum-cobalt

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Zhang, B., Sheng, T., Wang, Y., Qu, X., Zhang, J., Zhang, Z., Liao, H., Zhu, F., Dou, S., Jiang, Y. & Sun, S. (2017). Platinum-Cobalt Bimetallic Nanoparticles with Pt Skin for Electro-Oxidation of Ethanol. *ACS Catalysis*, 7 (1), 892-895.

Authors

Binwei Zhang, Tian Sheng, Yunxiao Wang, Xi-Ming Qu, Jun-Ming Zhang, Zong-Cheng Zhang, Hong-Gang Liao, Fu-Chun Zhu, Shi Xue Dou, Yan-Xia Jiang, and Shi-Gang Sun

Platinum–Cobalt bimetallic nanoparticles with Pt skin for electro-oxidation of ethanol

Bin-Wei Zhang^{a,b}, Tian Sheng^a, Yun-Xiao Wang^b, Xi-Ming Qu^a, Jun-Ming Zhang^a, Zong-Cheng Zhang^a, Hong-Gang Liao^a, Fu-Chun Zhu^a, Shi-Xue Dou^b, Yan-Xia Jiang^{a,*} and Shi-Gang Sun^{a,*}

^a, State Key Laboratory of Physical Chemistry of Solid Surfaces, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

^b, Institute for Superconducting and Electronic Materials, Australian Institute of Innovative Materials, University of Wollongong, Innovation Campus, Squires Way, North Wollongong, New South Wales 2500, Australia.

Supporting Information Placeholder

ABSTRACT: In order to maximize the Pt utilization in catalysts and improve catalytic processes, we report a convenient strategy for preparation Pt₃Co with Pt-skin structured bimetallic nanocatalysts directly supported on porous graphitic carbon. Notably, the thickness of the Pt-skin is only 1–2 atomic layers, about 0.5 nm. Surprisingly, the bimetallic nanocatalysts composed of Pt₃Co with Pt-skin are firstly used as ethanol electro-catalysts, with the mass activity of 0.79 mA μgPt⁻¹, which is 250% enhancement compared with commercial Pt/C (0.32 mA μgPt⁻¹). Based on the results of electrochemical *in-situ* Fourier transform infrared spectroscopy (FTIR) and density functional theory (DFT), a new ethanol electro-oxidation enhancement mechanism is proposed in which Pt₃Co with Pt-skin promotes partial oxidation of ethanol over C-C bond cleavage, thereby resulting in higher CH₃COOH production than CO₂ production.

Bimetallic nanoparticles play a vital role in energy conversion and storage, for instance supercapacitor, battery, fuel cell, and solar fuel ¹. Unlike monometallic nanoparticles, bimetallic nanoparticles ordinarily show better than the sum of its parts since they could create synergistic effect during their combination ². It is worth mentioning that electro-catalytic reactions only happen on electro-catalysts surface³. It is significant to investigate the surface composition of bimetallic catalysts thus a deeper understanding of electro-catalytic reaction mechanism, kinetics and energy efficiency would be produced.

Platinum equips with the attribute of excellent efficiency in electrocatalyst for ethanol electro-oxidation. Nevertheless, it is difficult to widely apply Pt in direct ethanol fuel cells (DEFCs) for both stationary and portable applications, since the barriers of the prices and scarcity of Pt. It is widely acknowledged that CH₃CH₂OH electro-oxidation involves two parallel pathways, the complete oxidation (CH₃CH₂OH + 3H₂O = 2CO₂ + 12H⁺ + 12e) and the incomplete oxidation (CH₃CH₂OH + H₂O = CH₃COOH + 4H⁺ + 4e). In addition, Pt catalyst is inefficient at breaking the C-C bond in ethanol oxidation. Considerable progress has been made towards improving ethanol electro-oxidation performance on Pt-based bimetallic electrocatalysts, such as alloying with Pd ⁴, SnO₂ ⁵, and Rh ⁶. Meanwhile, atomic steps, ledges, and kinks were proven to play a significant role in ethanol electro-oxidation in our previous work ⁷. And the Pt₃Ni catalysts show different catalytic activity in terms of oxygen reduction reaction when the sur-

face is tuned from Pt-skin to Ni-rich surface ⁸. Since the atomic steps, ledges, and kinks of Pt-skin catalysts are different from those of pure Pt catalysts, we synthesized Pt₃Co with a Pt-skin surface, supported on porous graphitic carbon (PC) (denoted as Pt₃Co@Pt/PC). Pt and Co precursors were reduced by controlled thermal treatment, and the Pt₃Co nanoparticles were well-dispersed on PC, even after high temperature treatment (see Supporting Information). The reason of formation of Pt-skin may be following this: firstly, at 300 °C during 3 h, platinum and cobalt precursors are reduced at forming gas (10 vol % H₂ in nitrogen), at this process platinum and cobalt precursors have been reduced. This process facilitates a surface segregation of Pt because it has a trend to form moderate segregation⁸. Further, while it was heated up to 700 °C for 3 h, the segregation of Pt happened on the surface and the high temperature provides H₂ enough energy to preferentially combine with Pt on the surface^{3a}, which process is like high temperature process to form Pt-skin on single crystal^{3c}. This study is the first exploration of ethanol electro-oxidation on Pt-skin of Pt₃Co/PC, and it exhibited superior activity. Atomic resolution high-angle annular dark field (HAADF) scanning transmission electron microscope (STEM) imaging, coupled with electrochemical *in-situ* FTIR spectroscopy, are used to confirm the thickness of the Pt-skin is 1–2 atomic layers, about 0.5 nm. *In-situ* FTIR and DFT give a new insight into breakage of the C-C bonds in ethanol on Pt₃Co@Pt/PC and Pt/C. In contrast to Pt/C, the Pt-skin of Pt₃Co@Pt/PC is easier to produce acetic acid for ethanol electro-oxidation.

Figure 1a presents the atomic-resolution annular dark-field (ADF)-STEM image of Pt₃Co@Pt/PC. It should be pointed out that the relationship between image's pixel intensity and the element number Z is the proportion on the whole in the HAADF imaging mode ⁹, so compared with the Co columns, the Pt columns would show higher intensity, thus leading to higher Pt intensity than that of Pt₃Co ⁸. Therefore, we examined four sites of Pt₃Co@Pt/PC. The intensities of the four sites in Pt₃Co@Pt/PC were determined by intensity analysis, which are shown in Figure 1b-e, respectively. Both sites L1 and L3 have 2 Pt atomic layers; sites L2 and L4 have 1 Pt atomic layer. As shown in the Figure 1f of the high-resolution TEM (HRTEM), the *d*-spacing of the edge is measured to be 2.27 Å, which is consistent with Pt (111) ¹⁰, and the *d*-spacing of the center is ~ 2.22 Å, which could correspond to Pt₃Co(111) ¹¹. It indicates that the Pt₃Co@Pt/PC is Pt-skin surface; the center is Pt₃Co alloy. An ADF-STEM image of a nanoparticle

is shown in figure 2a, which is spectroscopically imaged. The Pt element and Co element projected distributions in this particle in figure 2b-c. The composite image of Pt versus Co (Figure 2d) suggested that the surface of this nanoparticle contains more amount of Pt than Co. Furthermore, Figure 2e presents the corresponding line-profile analysis from figure 2d shown by the arrow, which confirms that the thickness of Pt-skin is ~ 0.5 nm, corresponding to 2 atomic layers, consisting with the ADF results.

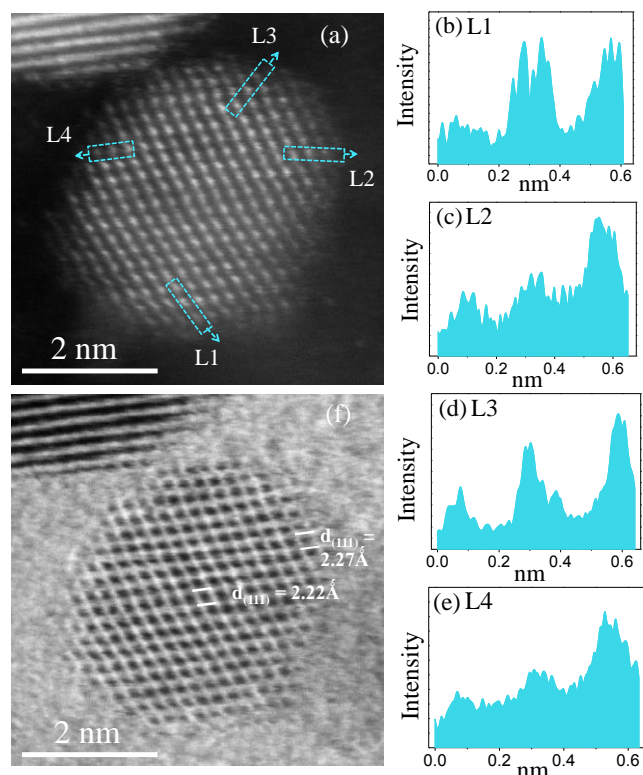


Figure 1(a) Atomic-resolution ADF-STEM image of $\text{Pt}_3\text{Co@Pt/PC}$, with the intensity of sites L1, L2, L3, and L4 shown in (b)–(e); (f) HRTEM image of $\text{Pt}_3\text{Co@Pt/PC}$.

The TEM image of $\text{Pt}_3\text{Co@Pt/PC}$ (Figure S2a in the Supporting Information) clearly shows that the $\text{Pt}_3\text{Co@Pt}$ nanoparticles are well dispersed with a high loading on PC. The average diameter of $\text{Pt}_3\text{Co@Pt}$ nanoparticles (Figure S2b) is evaluated to be 3.06 ± 0.86 nm from 200 nanoparticles. The X-ray diffraction (XRD) of $\text{Pt}_3\text{Co@Pt/PC}$ and Pt/C (Johnson Matthey) are shown in figure S3. The broad peaks near 25° of two catalysts are assigned to carbon; peaks at 40.3° , 46.8° , 68.2° , 82.7° of $\text{Pt}_3\text{Co@Pt/PC}$ are agreement with that of Pt/C, which present Pt face-centered cubic (fcc) features. Compared to Pt/C, all broad diffraction peaks of $\text{Pt}_3\text{Co@Pt/PC}$ are at high angles, because Co atoms are incorporated into the Pt fcc structure, forming Pt_3Co alloy¹².

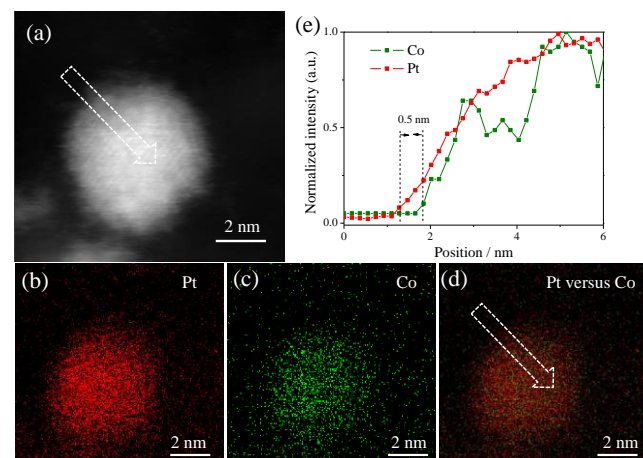


Figure 2(a) ADF-STEM image of $\text{Pt}_3\text{Co@Pt/PC}$ nanoparticle. (b-d) 2D electron energy loss spectroscopic mapping of Pt (red), Co (green), and the composite image of Pt vs Co. (e) Line-profile analysis from the indicated area of (a) and (d), demonstrating about 0.5 nm Pt skin thickness.

Cyclic voltammograms (CVs) of $\text{Pt}_3\text{Co@Pt/PC}$ and Pt/C are shown in Figure S4a, where the Pt/C exhibits the well-known hydrogen adsorption and desorption of pure Pt nanoparticles dispersed on carbon black in 0.1 M HClO_4 solution. In contrast, the CV of $\text{Pt}_3\text{Co@Pt/PC}$ does not show any apparent hydrogen adsorption and desorption, which is probably because the presence of Co in the $\text{Pt}_3\text{Co@Pt/PC}$ results in reduced hydrogen adsorption and desorption capacity. CO_{ad} stripping curves of two catalysts are shown in Figure S4b. The ratio of integrated charges ($Q_{\text{CO}} / 2Q_{\text{H}}$) between CO stripping (Q_{CO}) and under potential deposition of hydrogen H_{upd} (Q_{H}) is calculated to be 1.54 and 1.10 for $\text{Pt@Pt}_3\text{Co/PC}$ and Pt/C, respectively, in table S2. This relationship is in good agreement with the Pt-skin structure¹³.

On pure Pt, electro-oxidation of formic acid would form poisoning intermediates (CO_{ad}) via “dual pathway” because the CO poisoning takes place on at least two consecutive Pt surface sites¹⁴. For $\text{Pt}_3\text{Co@Pt/PC}$, the surface is Pt; so HCOOH may form adsorbed CO (CO_{ad}) through the dual pathway mechanism on $\text{Pt}_3\text{Co@Pt/PC}$ ⁸. Figure S5a shows the CVs of Pt/C and $\text{Pt}_3\text{Co@Pt/PC}$ in 0.1 M $\text{HCOOH} + 0.1$ M HClO_4 solution. The $\text{Pt}_3\text{Co@Pt/PC}$ oxidation of HCOOH is similar to that of Pt/C, which also has two anodic peaks. This suggests that both $\text{Pt}_3\text{Co/PC}$ (Pt-skin) and Pt/C operate via the dual pathway mechanism poisoned by CO_{ad} . Electrochemical *in-situ* FTIR spectra of HCOOH oxidation are shown in Figure S5b and S5c. Reference spectrum potentials are collected at -0.25 V, and working spectrum potentials vary from -0.20 to 0.70 V (0.1 V interval). The band at 2345 cm^{-1} is a characteristic peak of CO_2 asymmetric stretching vibration that originates from direct HCOOH oxidized and CO_{ad} oxidized, which can be observed in both catalysts. The band at 2050 cm^{-1} corresponds to linearly bonded CO (CO_{L}), which goes through the poisoning route. It is noteworthy that CO_{L} could be found clearly for both $\text{Pt}_3\text{Co@Pt/PC}$ and Pt/C, which indicates that oxidation of HCOOH via the poisoning route on $\text{Pt}_3\text{Co@Pt/PC}$ as well. This conclusion furtherly implies that $\text{Pt}_3\text{Co@Pt/PC}$ has a Pt-skin⁸. Moreover, the activity of $\text{Pt}_3\text{Co@Pt/PC}$ is better than that of Pt/C; it attributes that the sub-surface layers of Co atoms may affect the electronic structure of the outermost Pt-skin.

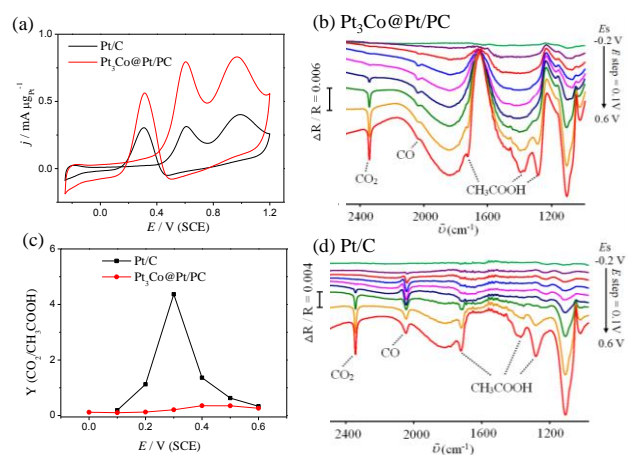


Figure 3(a) Cyclic voltammograms (CVs) of $\text{Pt}_3\text{Co@Pt/PC}$ and Pt/C in 0.1 M $\text{CH}_3\text{CH}_2\text{OH} + 0.1$ M HClO_4 solution, 50 mV s^{-1} . *In-situ* mass spectroscopy (MS) FTIR spectra of (b)

Pt₃Co@Pt/PC and (d) Pt/C for CH₃CH₂OH oxidation in 0.1 M CH₃CH₂OH + 0.1 M HClO₄. (c) Ratio of integrated intensities of CO₂ and intensities CH₃COOH as a function of working potentials of the two electrocatalysts.

Electrocatalytic oxidation of ethanol in acidic solution (0.1 M HClO₄ + 0.1 M CH₃CH₂OH) was used to study the catalytic property of the Pt₃Co@Pt/PC, as shown in Figure 3a. It is obvious that Pt₃Co@Pt/PC and Pt/C show similar CV curves, which display two peaks at 0.60 V and 0.96 V, corresponding to the well-known ethanol electro-oxidation^{6b}. The first peak (at 0.60 V) is ascribed to formation of CH₃CHO, CH₃COOH and CO₂; the following peak ~ 0.96 V is assigned to CH₃COOH. Significantly, the current density of Pt₃Co@Pt/PC is 0.79 mA μg_{Pt}⁻¹ at 0.60 V, which is 2.5 times as high as that of Pt/C (0.32 mA μg_{Pt}⁻¹). Figure S6 shows the current-time curves at 0.45 V on Pt₃Co@Pt/PC and Pt/C at room temperature. After 3600 s, the activity of Pt₃Co@Pt/PC is still better than that of Pt/C, regardless of its mass activity or specific activity.

To understand the impact of the Pt-skin surface of Pt₃Co@Pt/PC electro-catalyst on ethanol, *in-situ* FTIR contributes to recognize the intermediate and final products to identify the selectivity towards CH₃CH₂OH electro-oxidation, as shown in Figure 3b (Pt₃Co@Pt/PC) and 3d (Pt/C). The signature peak of CO₂ (~2345 cm⁻¹) corresponds to complete oxidation of CH₃CH₂OH, which represents the breaking of the C-C bond in CH₃CH₂OH oxidation. The band at ~1720 cm⁻¹ is attributed to the C=O bond's stretching vibration in CH₃CHO and CH₃COOH, which indicates incomplete electro-oxidation of CH₃CH₂OH. The characteristic absorption band of C-O stretching in CH₃COOH at 1280 cm⁻¹ is typically applied to quantitative analysis of CH₃COOH. Remarkably, lines for bound CO (CO_L) at 2050 cm⁻¹ could be found in both the Pt/C and the Pt₃Co@Pt/PC catalysts, which further indicate that Pt₃Co@Pt/PC possesses a Pt skin. Figure S7 shows the variation of the integrated intensities of the 2345 cm⁻¹ band (CO₂) and the 1280 cm⁻¹ band (C-O) corresponding to potential for Pt₃Co/PC (Pt-skin) and commercial Pt/C samples. To investigate the capability for C-C bond breaking in CH₃CH₂OH, we plot the ratio of integrated intensities (*I*) associated with CO₂ (total electro-oxidation) and CH₃COOH (partial electro-oxidation) as a function of working potentials (Figure 3c). It can be clearly seen that the ratio of *I*_{CO₂}/*I*_{CH₃COOH} firstly raises but reduces subsequently when the applied potentials increases. Compared with Pt/C, the value of *I*_{CO₂}/*I*_{CH₃COOH} for Pt₃Co@Pt/PC is low, which suggests that the main product of Pt₃Co@Pt/PC is CH₃COOH. Pt is a poor catalyst for ethanol oxidation; adding Sn into Pt (PtSn) could ensemble electro-oxidize CH₃CH₂OH to CH₃COOH, which is difficult to break the C-C bond¹⁵. When Sn is added on the surface of Pt, the alloy not only could minimize the poisoning effects but also improve the activity towards ethanol electro-oxidation^{15a,16}. As for Sn, it could increase formation of OH species at lower potential, which could oxidize CH₃CHO to produce more CH₃COOH¹⁵. The comparison Pt₃Co@Pt/PC with Pt-Sn catalyst is listed in table S3. It could be found that specific activity of Pt₃Co@Pt/PC at 0.3 V is lower than PtSn^{15b} and Pt₇Sn₃¹⁷. It may be attributed that the surface of Pt₃Co@Pt/PC is Pt-skin, however, the surface of PtSn^{15b} and Pt₇Sn₃¹⁷ have Sn, which help formation of OH species.

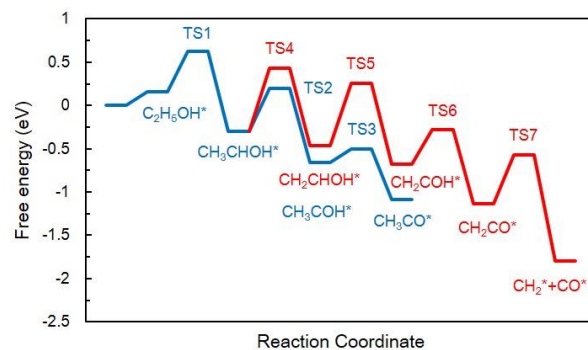


Figure 4 Energy profiles of ethanol electrooxidation on the stepped Pt₃Co(211) surface.

The reaction mechanism of CH₃CH₂OH electro-oxidation on the stepped Pt₃Co(211) surface with a Pt-skin structure were revealed by DFT calculations. The free energy is displayed in Figure 4 and all the calculated data and the optimized structures are shown in Figure S8 and S9. According to the previous theoretical investigation, CH₃CHOH* can break the α-C-H bond or the β-C-H bond, and the barrier difference between them can be used to evaluate the CH₃COOH/CO₂ selectivity¹⁸. On stepped Pt₃Co(211) surface, CH₃CHOH* strongly prefers to break the α-C-H bond, producing CH₃COH* with a barrier being 0.5 eV (transition state(TS) 2,) rather than breaking the β-C-H bond with a barrier being 0.73 eV (TS 4). Afterwards, CH₃CO* readily forms after overcoming a barrier of 0.16 eV to break the O-H bond in CH₃COH* (red line). CH₃CO* is rather stable on the surface and would be oxidized to CH₃COOH* at high potentials, leading the partial electro-oxidation of CH₃CH₂OH to CH₃COOH dominated, which is in consistent with the *in situ* FTIR observations. In the other way to break C-C bond starting from CH₂CHOH*, the C-H bond breaking barrier is 0.72 eV to yield CH₂COH*, and the O-H bond breaking barrier is 0.4 eV for the formation of CH₂CO*. CH₂CO* is a reasonable precursor to split the C-C bond to CH₂* and CO* with a low barrier of 0.57 eV (blue line).

In summary, the Pt₃Co@Pt/PC with the Pt-skin structure was successfully prepared by a sample controlled thermal treatment method. A unique Pt-skin structure is confirmed by a series of complementary techniques. The Pt-skin is 1-2 atomic layers with thickness of about 0.5 nm. Benefiting from the bimetallic synergic effect and unique structural advantages, the mass activity of 0.79 mA μg_{Pt}⁻¹ is achieved on Pt₃Co@Pt/PC, which is 2.5 times as high as that of Pt/C towards ethanol electro-oxidation. Via *in-situ* FTIR spectra and DFT, ethanol prefers to be broken α-C-H bond producing CH₃COH* rather than breaking the β-C-H bond yielding CH₂COH* on Pt₃Co@Pt/PC.

ASSOCIATED CONTENT

Supporting Information

Experimental details, related characterization, and supporting results and discussion. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

yxjiang@xmu.edu.cn and sgsun@xmu.edu.cn

ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (Grant Nos. 21273180, 21321062, 21361140374, 2015CB932303, 51421002, XDB07030200, 2014CB921002, and 51522212). The authors also acknowledge Dr. Tania Silver for her critical reading.

REFERENCES

- [1] a) E. E. Benson, C. P. Kubiak, A. J. Sathrum, J. M. Smieja, *Chem Soc Rev* **2009**, *38*, 89-99; b) M. Sankar, N. Dimitratos, P. J. Miedziak, P. P. Wells, C. J. Kiely, G. J. Hutchings, *Chem Soc Rev* **2012**, *41*, 8099-8139; c) M. R. Gao, Y. F. Xu, J. Jiang, S. H. Yu, *Chem Soc Rev* **2013**, *42*, 2986-3017.
- [2] a) D. Wang, Y. Yu, H. L. Xin, R. Hovden, P. Ercius, J. A. Mundy, H. Chen, J. H. Richard, D. A. Muller, F. J. DiSalvo, H. D. Abruña, *Nano Letters* **2012**, *12*, 5230-5238; b) C. Wang, N. M. Markovic, V. R. Stamenkovic, *ACS Catalysis* **2012**, *2*, 891-898.
- [3] a) H. Liao, A. Fisher, Z. J. Xu, *Small* **2015**, *11*, 3221-3246; b) D. Volpe, E. Casado-Rivera, L. Alden, C. Lind, K. Hagerdon, C. Downie, C. Korzeniewski, F. J. DiSalvo, H. D. Abruña, *Journal of The Electrochemical Society* **2004**, *151*, A971; c) V. R. Stamenkovic, B. Fowler, B. S. Mun, G. F. Wang, P. N. Ross, C. A. Lucas, N. M. Markovic, *Science* **2007**, *315*, 493-497.
- [4] a) C. Zhu, S. Guo, S. Dong, *Advanced Materials* **2012**, *24*, 2326-2331; b) K. Sasaki, H. Naohara, Y. Cai, Y. M. Choi, P. Liu, M. B. Vukmirovic, J. X. Wang, R. R. Adzic, *Angewandte Chemie, International Edition* **2010**, *49*, 8602-8607.
- [5] W. Du, G. Yang, E. Wong, N. A. Deskins, A. I. Frenkel, D. Su, X. Teng, *J Am Chem Soc* **2014**, *136*, 10862-10865.
- [6] a) A. Kowal, M. Li, M. Shao, K. Sasaki, M. B. Vukmirovic, J. Zhang, N. S. Marinkovic, P. Liu, A. I. Frenkel, R. R. Adzic, *Nature Materials* **2009**, *8* 325; b) L. Rao, Y.-X. Jiang, B.-W. Zhang, Y.-R. Cai, S.-G. Sun, *Physical Chemistry Chemical Physics* **2014**, *16*, 13662.
- [7] N. Tian, Z.-Y. Zhou, S.-G. Sun, Y. Ding, Z. L. Wang, *Science* **2007**, *316*, 732-735.
- [8] B.-W. Zhang, Z.-C. Zhang, H.-G. Liao, Y. Gong, L. Gu, X.-M. Qu, L.-X. You, S. Liu, L. Huang, X.-C. Tian, R. Huang, F.-C. Zhu, T. Liu, Y.-X. Jiang, Z.-Y. Zhou, S.-G. Sun, *Nano Energy* **2016**, *19*, 198-209.
- [9] S. J. Pennycook, D. E. Jesson, *Ultramicroscopy* **1991**, *37*, 14-38.
- [10] S.-I. Choi, S. Xie, M. Shao, J. H. Odell, N. Lu, H.-C. Peng, L. Protsailo, S. Guerrero, J. Park, X. Xia, J. Wang, M. J. Kim, Y. Xia, *Nano Letters* **2013**, *13*, 3420-3425.
- [11] S. I. Choi, R. Choi, S. W. Han, J. T. Park, *Chemistry* **2011**, *17*, 12280-12284.
- [12] D. Wang, H. L. Xin, R. Hovden, H. Wang, Y. Yu, D. A. Muller, F. J. DiSalvo, H. D. Abruña, *Nat Mater* **2013**, *12*, 81-87.
- [13] a) D. F. van der Vliet, C. Wang, D. Li, A. P. Paulikas, J. Greeley, R. B. Rankin, D. Strmcnik, D. Tripkovic, N. M. Markovic, V. R. Stamenkovic, *Angewandte Chemie, International Edition* **2012**, *51*, 3139-3142; b) C. Chen, Y. J. Kang, Z. Y. Huo, Z. W. Zhu, W. Y. Huang, H. L. L. Xin, J. D. Snyder, D. G. Li, J. A. Herron, M. Mavrikakis, M. F. Chi, K. L. More, Y. D. Li, N. M. Markovic, G. A. Somorjai, P. D. Yang, V. R. Stamenkovic, *Science* **2014**, *343*, 1339-1343.
- [14] a) S. Park, Y. Xie, M. J. Weaver, *Langmuir* **2002**, *18*, 5792-5798; b) E. Leiva, T. Iwasita, E. Herrero, J. M. Feliu, *Langmuir* **1997**, *13*, 6287-6293.
- [15] a) Q. Wang, G. Q. Sun, L. H. Jiang, Q. Xin, S. G. Sun, Y. X. Jiang, S. P. Chen, Z. Jusys, R. J. Behm, *Physical chemistry chemical physics P* **2007**, *9*, 2686-2696; b) L. Rao, B.W. Zhang, Y. Y. Li, Y. X. Jiang, S. G. Sun, *Journal of Electrochemistry*, **2014**, *20*, 395-400.
- [16] a) V. Del Colle, J. Souza-Garcia, G. Tremiliosi-Filho, E. Herrero, J. M. Feliu, *Physical chemistry chemical physics* **2011**, *13*, 12163-72; b) L. Jiang, L. Colmenares, Z. Jusys, G. Q. Sun, R. J. Behm, *Electrochim. Acta* **2007**, *53* (2), 377-389.
- [17] W. Du, G. Yang, E. Wong, N. A. Deskins, A. I. Frenkel, D. Su, X. Teng, *J Am Chem Soc* **2014**, *136*, 10862-5.
- [18] a) T. Sheng, W. F. Lin, C. Hardacre, P. Hu, *Phys. Chem. Chem. Phys.*, **2014**, *16*, 13248-13254; b) T. Sheng, W. F. Lin, S. G. Sun, *Phys. Chem. Chem. Phys.*, **2016**, *18*, 15501-15504.

2-D S nanosheets were successfully in-situ grew on Cu foam current collector. When applied as cathode for room room-temperature Na-S batteries, the S cathode delivers ultrahigh electroactivity with the highest initial discharge/charge capacity of 3189/1403 mAh g⁻¹, which shows great potential to realize high-capacity S cathode.

