Electronic Supplementary Information

Facile approach to enhance the Pt utilization and CO-tolerance of Pt/C catalyst by physically mixing with transition metal oxides nanoparticles

Jingyu Xi,[a,b] Jianshe Wang,[a,b] Lihong Yu,[a] Xinping Qiu*[a,b] and Liquan Chen[a,b]

[a] Key Lab of Organic Optoelectronics and Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing 100084, China. E-mail: qiuxp@tsinghua.edu.cn (X. Qiu), xijingyu@gmail.com (J. Xi); Fax: 86-10-62794234

[b] Lab of Advanced Power Sources, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China.

Experimental Section

Preparation of transition metal oxides (TMO) nanoparticles

All transition metal oxides (TMO) nanoparticles used in this work were prepared by molten salt method as described in Ref. (1) and (2). Cerium nitrate, zirconium nitrate, and tetrabutyl titanate were used as precursors for preparation of CeO_2, ZrO_2, and TiO_2, respectively. For a typical synthesis process, $K_2C_2O_4$ solution was added drop-wise into the cerium nitrate solution with constant stirring to attain a pH value of 10. The resultant precipitation was filtrated and washed with deionized water and ethanol repeatedly, and then dried at 80 ^{o}C for 12 h. This precipitation and KNO_3 were mixed with a mortar and pestle at molar ratio of 1:3. The mixtures were calcined at 500 ^{o}C for 3 h, and then cooled to ambient temperature. The products were immersed in deionized water, washed and filtered repeatedly to remove the residual fluxes. Finally, the products were dried at 120 ^{o}C to obtain the CeO_2 nanoparticles. The morphologies of the TMO nanoparticles were examined by TEM (JEOL model JEM-1200EX). As shown in Figure S2, the average particle size is 9.5 nm, 4.6 nm, and 10.1 nm for CeO_2, ZrO_2, and TiO_2, respectively.

Working electrode preparation

The catalyst ink was prepared by mixing the Pt/C catalyst (E-Tek, 20 wt.% Pt) with perfluorsulfonic acid solution (5 wt.%, Nafion®, DuPont), ethylene glycol (EG) and deionized water ultrasonically. For the case of Pt/C+TMO, TMO nanoparticles were first dispersed in deionized water ultrasonically, and then mixed with Pt/C, Nafion®, and

EG ultrasonically. The resulting slurry was spreaded onto a gold patch of ca. 1.0 cm^2 (1×1 cm). Then the electrode was dried at 80 ^{o}C in air with the total catalyst loadings of about 0.1 mg Pt/cm^2.

Characterization

The morphologies of the Pt/C catalyst and TMO nanoparticles were examined by TEM (JEOL model JEM-1200EX). The catalyst structure of Pt/C+TMO was observed using a scanning electron microscope (SEM, LEO1530), and EDS analysis was used to analyze the element distribution in the catalyst architecture.

Electrochemical measurements

Electrochemical measurements were carried out in a three electrode cell using a Solartron SI1287 workstation at 25 ºC. A saturated calomel electrode (SCE) and Pt gauze were used as reference and counter electrodes, respectively. All electrode potentials in this paper are referred to the SCE. A solution of in 1 M alcohol + 1 M $HClO_4$ was used as electrolyte. All the reagents used were of analytical grade. Several activation scans were performed until reproducible voltammograms were obtained. Cyclic voltammograms were recorded in the potential range -0.2 to 1.0 V vs. SCE at a scan rate of 50 mV s^{-1}. The oxidation of preadsorbed CO was measured by CO stripping voltammetry in 1M $HClO_4$ solution at a scan rate of 10 mV s^{-1}. All the recorded currents are corrected for the weight percentage of the platinum in catalysts. The experimental error during CV test in this work is within 5 mV.

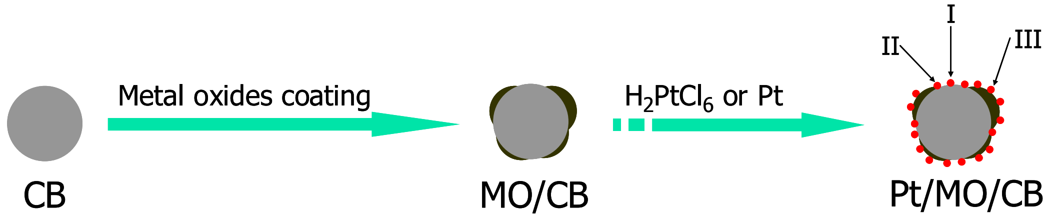

Figure S1 Schematic representation of the preparation process of Pt/MO/C catalyst. First, metal oxide (MO) was coated on the surface of carbon black (CB) by microwave irradiation method[3] or co-precipitation method[4] to obtain the MO/CB support. It is hard to control the size, shape, morphology, and thickness of the MO on the surface of CB in this step. Secondly, Pt nanoparticles were deposited on MO/CB to obtain the Pt/MO/CB catalyst. Three types of Pt species exit in the Pt/MO/CB catalyst, as shown in the figure.

(I) Pt deposits on the surface of CB, which is the same as pristine Pt/C catalyst.

(II) Pt deposits on the interface of CB and MO, which causes the most active site of the catalyst, when Pt contact well with CB and MO. According to the bifunctional mechanism, the OH_{ads} species on MO can transform CO-like poisoning species (CO_{ads}) on Pt to CO_2, releasing the active sites on Pt for further electrochemical reaction.

(III) Pt deposits on the surface of MO, which may be useless due to the bad electron conductivity of MO.

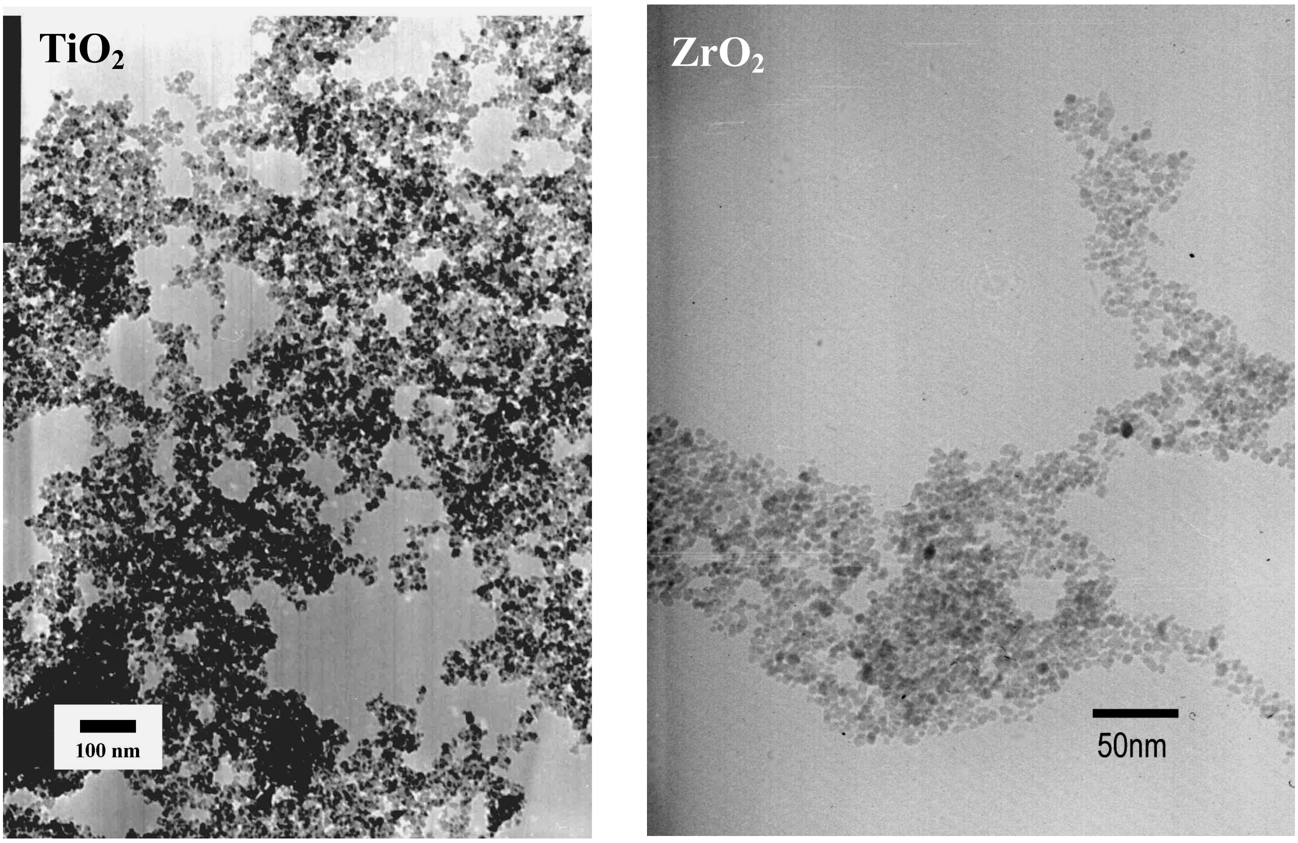

Figure S2 TEM images of TiO_2 (left) and ZrO_2 (right) nanoparticles prepared from molten salt method. The average particle size is 10.1 nm and 4.6 nm for TiO_2 and ZrO_2, respectively.

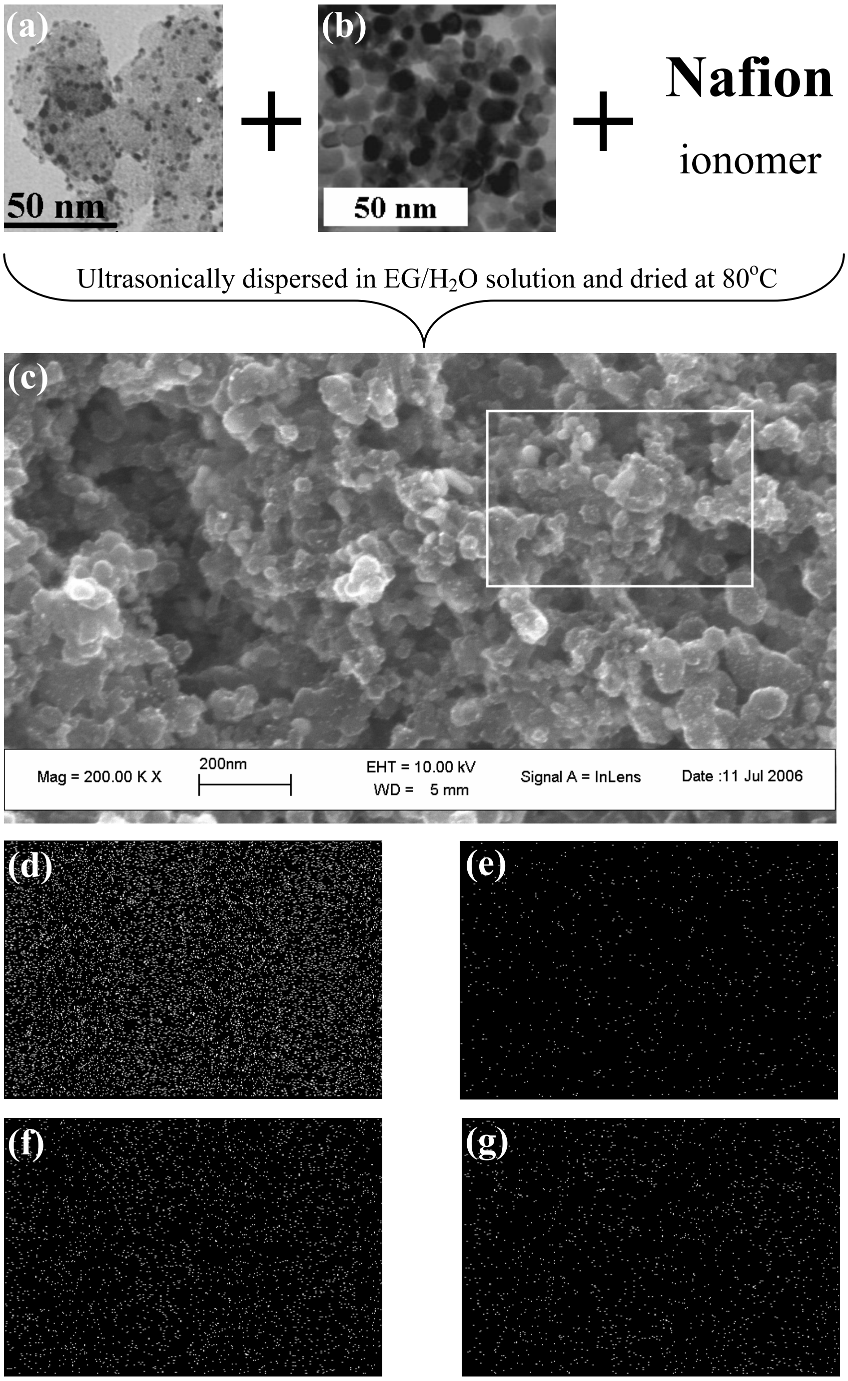

Figure S3. (a) TEM image of Pt/C (E-Tek, 20 wt.% Pt) catalyst; (b) TEM image of as prepared CeO_2 nanoparticles; (c) SEM image of the catalyst architecture of Pt/C+20wt.%CeO_2; (d)-(g) show the distribution of C, Pt, Ce, S element of the selective position in (c), which was measured by EDS, respectively.

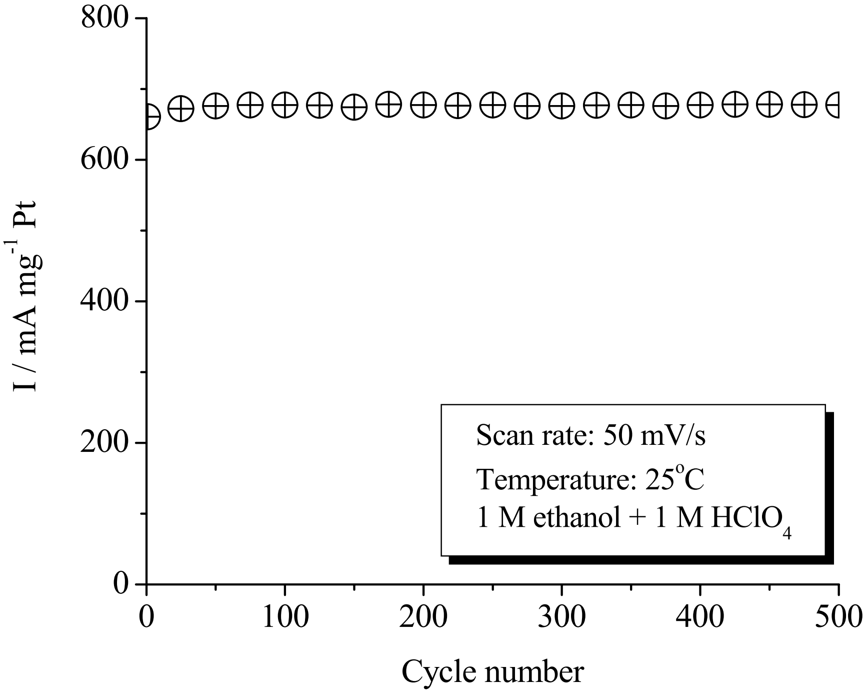

Figure S4. Stability of the Pt/C+20wt.%CeO_2 catalyst over 500 cycles of ethanol electrooxidation.

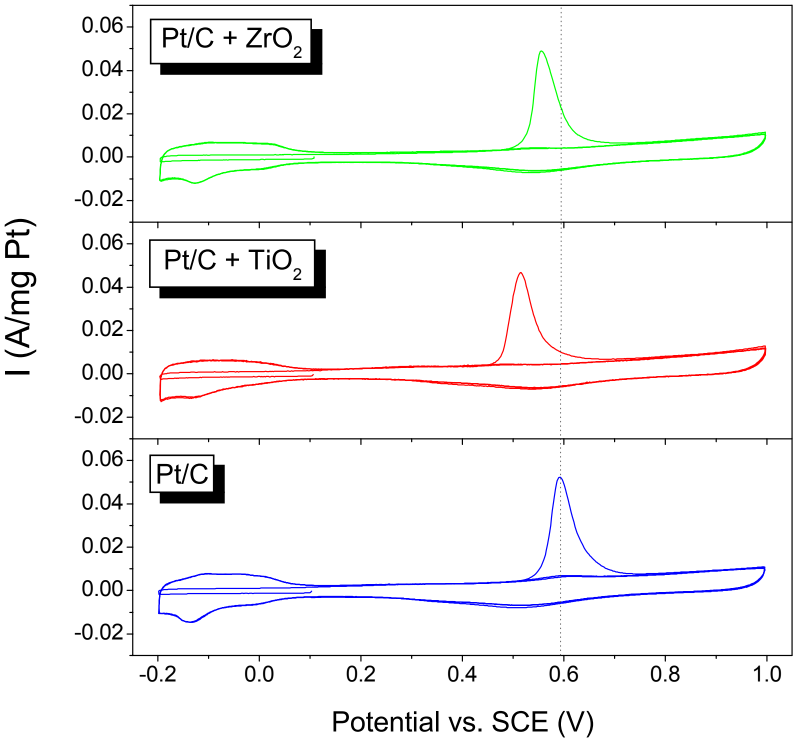

Figure S5. CO stripping voltammetry curves recorded at 25 °C in 1 mol/L $HClO_4$ in the potential range of -0.2 V to 1.0 V vs. SCE with a scan rate of 10 mV/s for Pt/C, Pt/C+20wt.%ZrO_2, and Pt/C+20wt.%TiO_2 catalysts. The CO was adsorbed at 0.1 V for 20 min, subsequently, the solution CO was removed by N_2 bubbling for 30 min maintaining at 0.1 V. Both Pt/C+20wt.%ZrO_2 and Pt/C+20wt.%TiO_2 show lower onset and peak potentials for CO oxidation compared with pristine Pt/C catalyst.

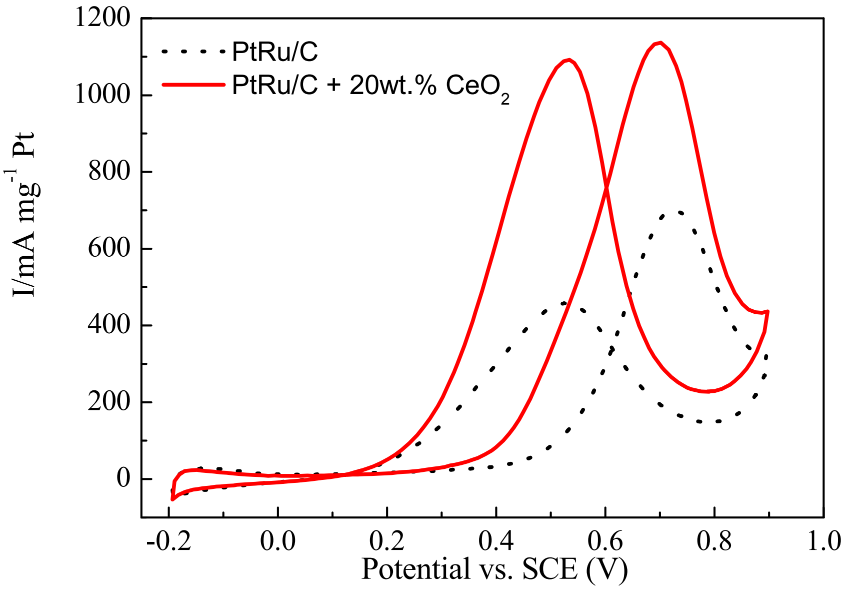

Figure S6. Cyclic voltammetry curves of methanol electro-oxidation at PtRu/C (E-TEK; 20 wt% on Vulcan, Pt:Ru=1:1) with and without CeO_2 nanoparticles recorded at 25 °C in 1 M methanol + 1 M $HClO_4$ in the potential range of -0.2 V to 0.9 V vs. SCE with a scan rate of 50 mV/s. Only the last voltammograms (the 50th scan) were used for comparison the catalytic activity of the specified catalysts.

References

(1) Liang H. Y.; Qiu X. P.; Zhang S. C.; He Z. Q.; Zhu W. T.; Chen L. Q. *Electrochem. Commun.* **2004**, *6*, 505-509.

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(4) Bai Y. X.; Wu J. J.; Xi J. Y.; Wang J. S.; Zhu W. T. Chen L. Q.; Qiu X. P. *Electrochem. Commun.* **2005**, *7*, 1087-1090.