Influence of nanostructured ceria support on platinum nanoparticles for methanol electrooxidation in alkaline media

Yunyun Zhou,[a] Christian L. Menéndez,[b] Maxime J.-F. Guinel,[b, c] Elizabeth C. Needels,[a] Ileana González-González,[b] Dichele L. Jackson,[a] Neil J. Lawrence,[a] Carlos R. Cabrera[b, *] and Chin Li Cheung[a, *]

[a] Department of Chemistry, University of Nebraska-Lincoln, Lincoln, NE 68588, USA.

[b] Department of Chemistry and NASA-URC Center for Advanced Nanoscale Materials, University of Puerto Rico, San Juan, Puerto Rico 00936-8377, USA.

[c] Department of Physics, College of Natural Sciences, University of Puerto Rico, San Juan, Puerto Rico 00936-8377, USA.

*Corresponding authors; e-mails: ccheung2@unl.edu; carlos.cabrera2@upr.edu

Electronic Supplemental Information
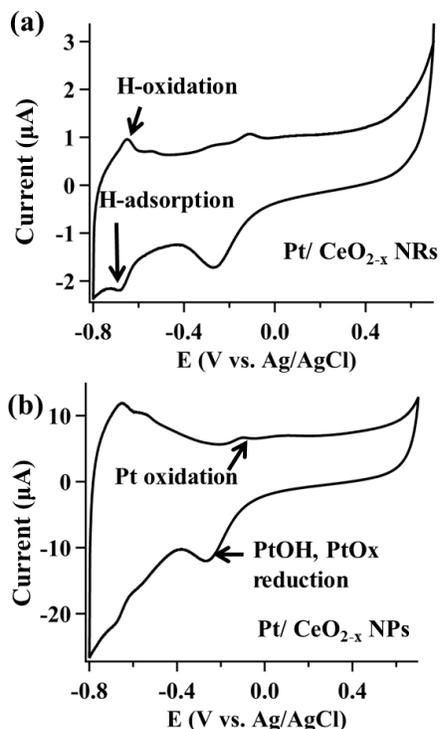
Fig. S1 Cyclic voltammetry of (b) Pt/ceria NRs and (b) Pt/ceria NPs catalysts in 0.50 M KOH at 50 mV/s. The hydrogen adsorption and Pt oxidation and PtOH reduction are identified.

The Pt active surface area was determined by determining the charge in the hydrogen adsorption potential region.[1, 2] Fig. S1 shows the typical CV curves of Pt/ceria in KOH solution. As it is well-known that ceria is not electroactive, peaks between -800 mV and -600 mV vs. Ag/AgCl are attributed to hydrogen adsorption. The large peak at -300 mV vs. Ag/AgCl on the cathodic scan is due to the reduction of Pt-OH and PtO_x to Pt^0. The peaks on the anodic scan are due to the formation of Pt hydroxide or oxides species from Pt^0.[3, 4] Typical active Pt surface areas of Pt/ceria NPs catalyst deposited on the glassy carbon (GC) electrodes were about 0.017 cm^2 and that for the Pt/ceria NRs were about 0.0037 cm^2. Pt/ceria NPs exhibited 4 times more active Pt surface area than that of Pt/ceria NRs, which enabled Pt/ceria NPs to provide more active Pt sites to oxidize methanol in the solution and hence display higher catalytic current density per Pt loading.

Table S1 The fitting parameters for Pt 4f XPS data of Pt/ceria NRs.

Peak	Binding Energy (eV)	FWHM (eV)
Pt^0 $(4f_{7/2})$	71.1	2.2
Pt-O-M $(4f_{7/2})$	71.7	0.6
Pt^{2+} $(4f_{7/2})$	72.8	1.7
Pt^{4+} $(4f_{7/2})$	73.6	1.5
Pt^0 $(4f_{5/2})$	74.6	1.7
Pt-O-M $(4f_{5/2})$	75.4	0.6
Pt^{2+} $(4f_{5/2})$	76.1	1.4
Pt^{4+} $(4f_{5/2})$	77.1	1.3

Table S2 The fitting parameters for Pt 4f XPS data of Pt/ceria NPs.

Peak	Binding Energy (eV)	FWHM (eV)
Pt^0 $(4f_{7/2})$	70.6	2.4
Pt-O-M $(4f_{7/2})$	71.9	0.4
Pt^{2+} $(4f_{7/2})$	72.7	2.1
Pt^0 $(4f_{5/2})$	74.1	2.0
Pt-O-M $(4f_{5/2})$	75.0	0.5
Pt^{2+} $(4f_{5/2})$	75.2	2.8

References
1. J. M. D. Rodriguez, J. A. H. Melian and J. P. Pena, *J. Chem. Educ.*, 2000, **77**, 1195-1197.
2. F. G. Will, *J. Electrochem. Soc.*, 1965, **112**, 451-455.
3. S. Basu, ed., *Recent Trends in Fuel Cell Science and Technology*, Springer & Anamaya, 2007.
4. L. M. Pan, Z. Y. Zhou, D. J. Chen and S. G. Sun, *Acta Phys-Chim Sin.*, 2008, **24**, 1739-1744.