

THE 2014 F. M. BECKET SUMMER RESEARCH FELLOWSHIP – SUMMARY REPORT

Support@Platinum - Nanoparticle Electrocatalytic Nanobowls

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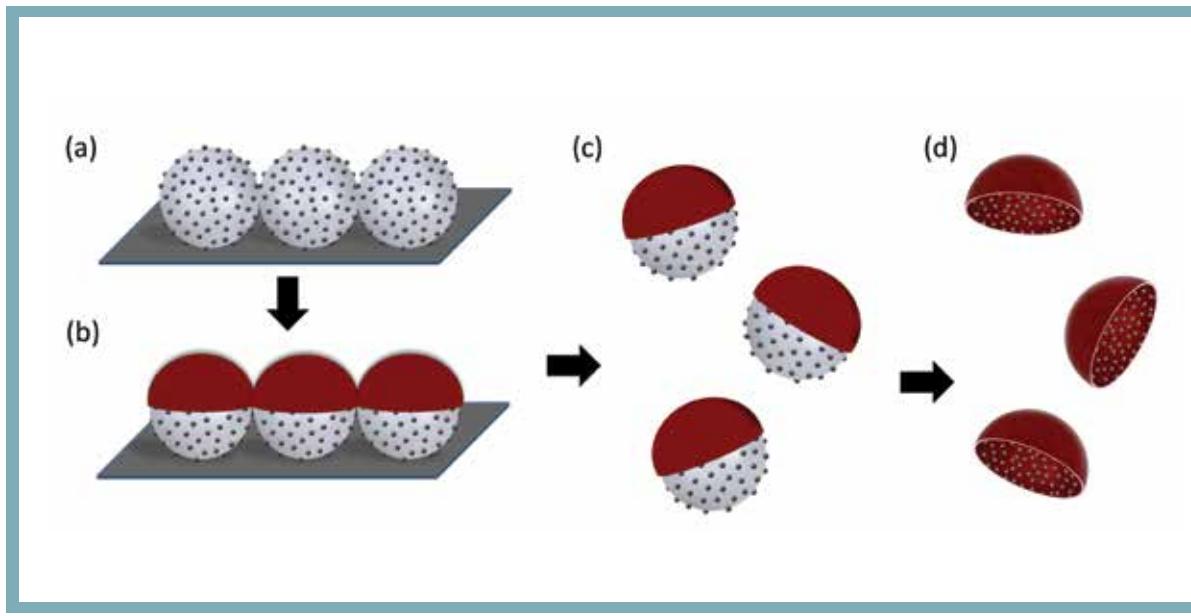
Electrocatalytic materials have become increasingly important over the past decade owing to their broad applicability to low emission and emission-free energy technologies, including fuel cell technology. Platinum is a great electrocatalyst due its generally good stability, high surface energy, electronic structure and interfacial properties.^{1–5} The morphology and chemical environment of Pt can have a substantial effect on its catalytic performance.^{2–7} Presently, carbon (C) black (high surface area C particles) is the most commonly used support for Pt nanoparticle (NP) electrocatalysts in low temperature polymer electrolyte membrane fuel cells (PEMFCs).⁴ This support provides a high surface area for dispersion of the Pt NPs and good electrical conductivity. Weak interaction between Pt NPs and the C support and oxidation of the C support under harsh fuel cell operating conditions leads to a loss of Pt catalysts and subsequent decrease in fuel cell performance. Alternative supports, such as metal oxides, are being pursued to improve the performance of fuel cell catalyst layers by increasing the stability of the Pt catalysts through favorable support interactions.^{6,7} This can increase the device lifetime and reduce the overall cost of the PEMFC.

The preparation of a new catalyst layer design that contained Pt NPs supported on metal or metal oxide nanobowls (NBs) was pursued in this study. These materials are hereafter referred to as support@PtNP NBs. A modular sacrificial template method (Scheme 1) was used to prepare the support@PtNP NBs.^{8–11} This new catalyst layer design offered a number of advantages over designs containing Pt NPs dispersed onto C black. These include: 1) optimization of catalyst-support interactions by tuning the composition of the support material; 2) fine tuning control over the distribution of Pt NPs over the surfaces of the NBs to mitigate degradation via aggregation and/or agglomeration; and 3) promoting porosity of the catalyst layer through the 3D morphology of the NB supports, which could improve reactant/product transport for efficient catalytic turnover.⁵ It was envisaged that these materials could also provide further insight into NP-support interactions through the preparation of materials that only differ in the support material composition, while maintaining the NP-support morphology (e.g., porosity of catalyst layer, Pt NP size and Pt NP distribution).

Using the described method, $\text{TiO}_x@\text{PtNP}$ NBs were prepared and characterized by electron microscopy (EM) (Fig. 1). Energy dispersive X-ray spectroscopy elemental maps (Fig. 1d) revealed that the Pt NPs were well dispersed over the inner surfaces of the TiO_x NB support. Nanobowl electrodes were also prepared by dispersing the NBs in Nafion® and casting the resulting catalyst suspension onto polished glassy carbon disks. The bowl-like shape of the NBs can be clearly seen in scanning EM images (Fig. 1e). Electrochemical characterization of this material, and preparation and characterization of other support@PtNP NB materials will be detailed in a subsequent report.

This new method for the preparation of supported nano-Pt catalysts could be readily expanded into other materials. The possible ability to easily tune electrochemical stability and activity of the Pt NPs by varying interactions with the support enables support@PtNP electrocatalytic nanobowls to have great potential for a variety of applications.

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SCHEME 1. Schematic describing the modular sacrificial template method used in the preparation of support@PtNP nanobowls. (a) Pt nanoparticle (NP) decorated polystyrene (PS) spheres are assembled onto a Si wafer.⁸ (b) The support material of interest is coated onto the surface of the assembled PS spheres using physical vapour deposition. (c) Pt NP decorated PS spheres with a partial coating of support material are released from the Si wafer support by sonication.⁷ (d) PS is dissolved in organic solvents under reflux conditions to reveal support@PtNP nanobowls.

Acknowledgments

I would like to thank The Electrochemical Society, the Natural Sciences and Engineering Research Council of Canada and my advisor, Dr. Byron Gates, for supporting this research. I would also like to thank Austin Lee, who has assisted in NB materials preparation.

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References

1. B. E. Conway and G. Jerkiewicz, *Electrochimica Acta*, **45**, 4075 (2000).
2. B. E. Hayden, *Accounts of Chemical Research*, **46**, 1858 (2013).
3. M. Nesselberger, M. Roefzaad, R. Faycal Hamou, P. Ulrich Biedermann, F. F. Schweinberger, S. Kunz, K. Schloegl, G. K. H. Wiberg, S. Ashton, U. Heiz, K. J. J. Mayrhofer and M. Arenz, *Nature Materials*, **12**, 919 (2013).
4. M. K. Debe, *ECS Trans.*, **45**(2), 47 (2012).
5. O.-H. Kim, Y.-H. Cho, S. H. Kang, H.-Y. Park, M. Kim, J. W. Lim, D. Y. Chung, M. J. Lee, H. Choe and Y.-E. Sung, *Nature Communications*, **4**, 2473 (2013).
6. Y.-J. Wang, D. P. Wilkinson and J. Zhang, *Chem. Rev.* **111**, 7625 (2011)
7. S. Y. Huang, P. Ganeshan, W. S. Jung, N. Cadirov, and B. N. Popov, *ECS Trans.*, **33**(1), 483 (2010)
8. J. C. Love, B. D. Gates, D. B. Wolfe, K. E. Paul and G. M. Whitesides, *Nano Letters*, **2**, 891(2002)
9. M. Xu, N. Lu, H. Xu, D. Qi, Y. Wang and L. Chi, *Langmuir*, **25**, 11216 (2009)
10. B. Kinkead, M. C. P. Wang, M. T. Y. Paul, A. Nazemi and B. D. Gates, submitted.
11. B. Kinkead, A. Ali, J. C. Boyer and B. D. Gates, *Mater. Res. Soc. Symp. Proc.*, **1546**, L001 (2013).

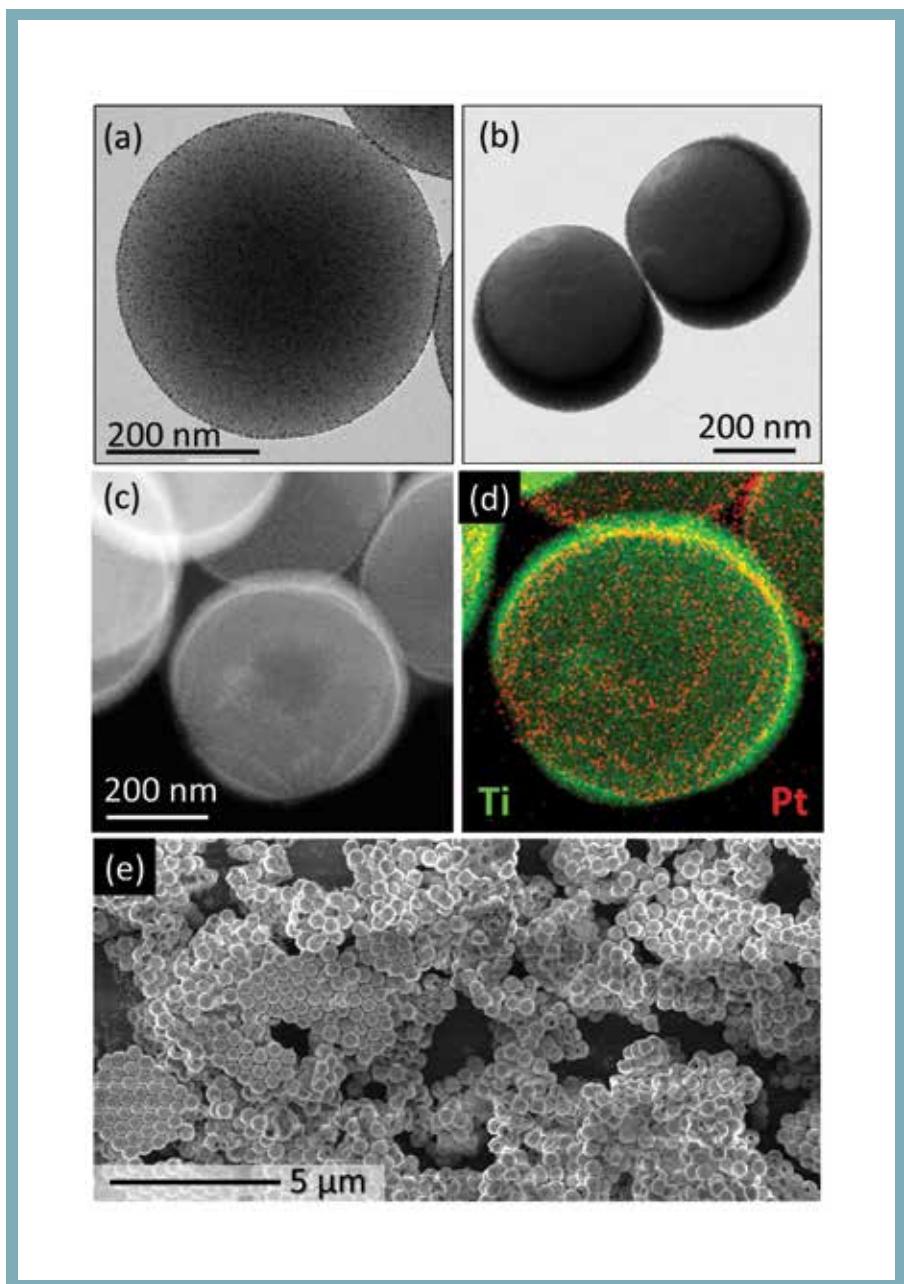


FIG 1. Electron microscopy analysis of $\text{TiO}_x@\text{PtNP}$ nanobowls. (a) Transmission electron microscopy (TEM) image of Pt NP decorated PS sphere template. (b) TEM image of Pt NP decorated PS sphere template partially coated with TiO_x . (c) Scanning TEM (STEM) image of $\text{TiO}_x@\text{PtNP}$ nanobowls. (d) Energy dispersive X-ray spectroscopy elemental map of a $\text{TiO}_x@\text{PtNP}$ nanobowl (as seen in (c) using STEM). (e) Scanning electron microscope image of a region of a $\text{TiO}_x@\text{PtNP}$ nanobowl electrode dispersed with Nafion polymer.