

October 31, 2022

Assistant Editor
Catalysts

Dear Referee

Thank you for your kind patience in waiting for our responses to the revision assignments by the reviewers. Below is the reference information for our submission and the responses to the referee's comments.

Journal: Catalysts

Manuscript ID: catalysts- 1978484

Title: " Optimization of SnPd Shell Configuration to Boost ORR Performance of Pt-Clusters Decorated CoOx@SnPd Core-Shell Nanocatalyst"

Author(s): Mingxing Cheng, Dinesh Bhalothia, Wei Yeh, Amisha Beniwal, Che Yan, Kuan-Wen Wang, Po-Chun Chen, Xin Tu, Tsan-Yao Chen *

We have properly responded to the revision comments and revised the manuscript accordingly.

If you have any concerns or more additional materials are required, please do not hesitate to contact me. I will be happy to provide it.

Sincerely yours,

Tsan-Yao Chen

COMMENTS FROM REVIEWER #1

Comment 1: Line 46: Please provide references for platinum catalyst being the benchmark.

Author reply: The authors appreciate the kind suggestion from the referee. As suggested the references have been added in the revised manuscript (*References 5-6*).

Comment 2: Line 86: Last paragraph of the introduction pretty much sums up the major conclusions of the paper. Authors are suggested to modify this to create a better transition from the existing literature to the scope of the present work

Author reply: The authors appreciate the kind suggestion from the referee. As suggested the last paragraph of introduction section has been updated in the revised manuscript.

“Although, M-core@Pd-shell structured NCs seem efficient design for next-generation heterogeneous catalysts with reduced Pt-loading, however, the high metal loading of Pd is still a severe issue. Moreover, recent studies also demonstrated that NCs comprising multiple metal-to-metal oxides or metal-metal heterogeneous interfaces boost the catalytic performances in various applications. By keeping such scenarios in view and inspired by previous studies, herein, we proposed a novel strategy for reducing the metal loading of noble metals (both Pt and Pd), while simultaneously enhancing their utilization. For doing so, we developed a multi-metallic NC comprising atomic scale Pt-clusters (1 wt.%) decorated CoO_x@SnPd Core-Shell structure (denoted as CSPP) with multiple heterogeneous interfaces. Furthermore, the ORR performance of CSPP NCs is optimized by manipulating the configuration of the SnPd shell by changing the Sn/Pd ratio from 0.5 to 2.0. In the optimum case, the CSPP NC with Sn/Pd ratio 0.5 (denoted as CSPP 1005) delivers the mass activity (MA) of 3034.7 mA mg_{Pt}⁻¹ at 0.85 V vs RHE in 0.1 M KOH electrolyte, which surpasses the commercial Johnson Matthey-Pt/C (J.M.-Pt/C; 20 wt.% Pt) catalyst (67 mA mg_{Pt}⁻¹) by is 45-times. The cross-referencing results of physical characterizations along with electrochemical analysis suggest that such high performance of CSPP 1005 NC originates from the potential synergism between surface-anchored atomic Pt-clusters, sub-nanometer PtPd nanoalloys, and adjacent SnPd domains, where Pt-clusters and PtPd nanoalloys promote the adsorption and subsequent splitting of O₂ molecules, while SnPd shell favours the OH⁻ relocation step. We envision that the present study is a novel and constructive exploration for designing highly active and affordable ORR catalysts. Hopefully, our findings can serve as guidance, providing new insights into the practical and efficient utilization of metals for the improvement of ORR performance.”

Comment 3: Line 107: What makes the sequential wet chemical reduction method robust? Please clarify in the text.

Author reply: The authors appreciate the kind suggestion from the referee. The proposed sequential wet chemical reduction method provides proper control of various parameters (impregnation temperature, impregnation time, reagent inlet sequence) during the crystal growth, which allows the preparation of material with desired size, shape and morphology. In addition, this one-pot

method is user-friendly and owing to its easiness and mild requirements (magnetic stirring), it can easily be adopted in the industry.

Comment 4: Line 137: It is not immediately clear from the text that figure S1 is supplementary. Please clarify.

Author reply: The authors appreciate the kind suggestion from the referee. As suggested the text has been simplified in the revised manuscript as “For fair explanation, the HRTEM image of CoOx@SnPd (denoted as CSP; i.e. without Pt decoration) is shown in the supplementary information (**Figure S1**).”

Comment 5: Figure 1: Need better labelling of all the pictures presented eg. red arrows and histograms. The conclusions based on the figures are not easily followed. Please modify for ease of understanding.

Author reply: The authors appreciate the kind suggestion from the referee. As suggested, the labelling in **Figure 1** has been updated. The same has been shown in **Figure R1**.

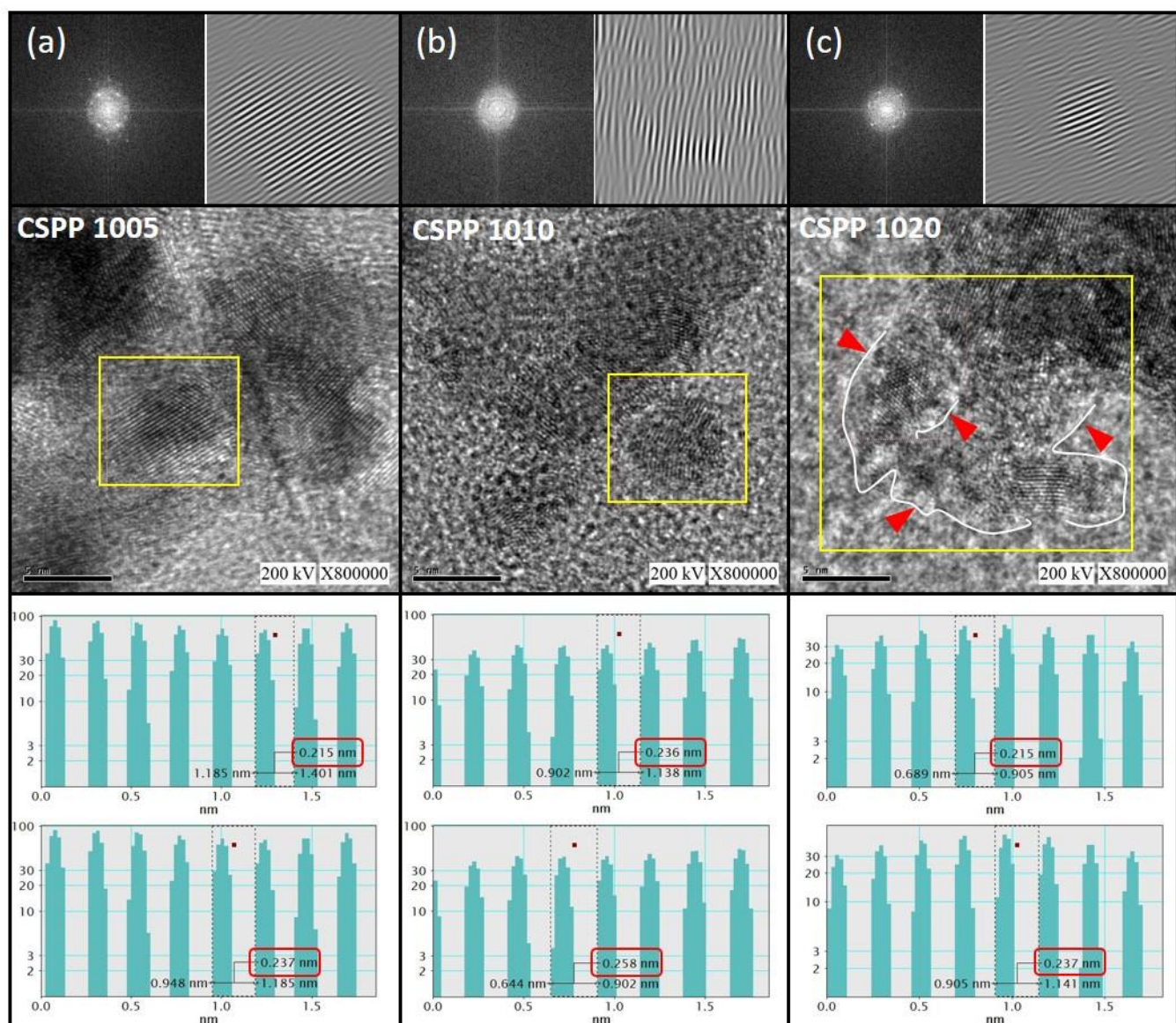


Figure R1. HRTEM images of CSPP NCs (a) CSPP 1005, (b) CSPP 1010 and (c) CSPP 1020. The d-Spacing values of experimental NCs are calculated by using Inverse Fourier Transform (IFT) images (upper right corners) and their corresponding line histograms (insets). Fourier transformation (FFT) patterns of the selected area in the HRTEM images are shown in the upper left corners.