NATIONAL ENERGY TECHNOLOGY LABORATORY
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U.S. DEPARTMENT OF ENERGY

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Title: "High-Performance Ligand-Protected Metal Nanocluster Catalysts for CO_2 Conversion Through Exposure of Undercoordinated Sites"

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Manuscript ID: catalysts-1649353

RESPONSE TO REVIEWER 2:

Comment 1: Authors should provide electron microscopic images (HRTEM) to understand the morphological features of the nanoclusters.

Author's Reply: Following the recommendation of the referee, the STEM images for monopalladium doped $Au_{25}(SR)_{18}^-$ and its parent counterpart are incorporated. They were combined with Figure 5 in the revised manuscript (Figures 5A-B, page 16). The line "From the scanning tunneling microscopy (STEM) images, both size and significant morphology can be ruled out upon monopalladium substitution in $Au_{25}(SR)_{18}^-$, namely, the monodispersed ~0.8 nm size was essentially preserved (Figures 5A-B)." is included on page 15 to represent the key takeaway from these images. No images are available for $Au_{25}(SR)_{18}^-$, $Au_{23}(SR)_{16}^-$ and its Cd doped version since STEM studies of these materials were not undertaken in our previous efforts.

Comment 2: Future perspectives portion should be more elaborative with more future application potential for this electroreduction process.

Author's Reply: Following the recommendation of the referee, the following paragraph was added in the Summary and Outlook portion (page 23): "From a practical standpoint, more research remains to be pursued for Au NC to realize its full potential. At present, the Au based electrocatalysts considered in this review have not been integrated to practical devices to open up the potential for low-cost and scalable deployment for CO_2 conversion to CO. Such setup would permit evaluation of the integrity of the materials at realistic conditions. Aside from the Au NC, membrane materials and electrocatalyst's support are integral to the device. To comprehend the potential role of these components in determining the outcome of the CO_2 conversion, it is necessary to invest effort into this aspect. The introduction of non-aqueous electrolytes plus the optimization of other conditions such as flow rate and pressure may significantly enhance the performance metrics as well. Thus, while there is always a need for fundamental research, a future focus that would pave the way for a practical CO_2 conversion to CO application is highly desirable."

Comment 3: Authors should compare the activity of these Au-nanoclusters with related nanocatalysts for the electroreduciton of CO_2.

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Author's Reply: We address this by adding the following passages in the revised manuscript:

Page 10: "It can successfully reduce CO_2 to CO beginning with an overpotential of -0.19 V (Figure 1A), indicating that $Au_{25}(SR)_{18}^-$ is superior to Au nanoparticles and bulk Au by 0.2 – 0.3 V. The FE for selective CO production reaches approximately 100% at −1.0 V (Figure 1B), which shows that almost every electron injected is harnessed in the conversion process. Additionally, the CO formation rate is 7−700 times higher than the conventional Au NPs and bulk Au electrodes at this industrially relevant potential."

Page 16: "Unlike conventional Au NPs and bulk Au electrodes, the results demonstrates that $Au_{24}Pd(SR)_{18}$ is capable of attaining 100% CO FE over a much wider potential range and a near-complete HER suppression up to −1.2 V."

Page 19: "Notably, $Au_{19}Cd_2(SR)_{16}^-$ demonstrates enhanced CO partial current density compared to other Au NC and Au NP.[60]. The ~ 40 mA/cm^2 value at -0.9 V is superior to the reported 2-18 mA/cm^2 for $Au_{44}(TBBT)_{28}$, $Au_{47}Cd_2(TBBT)_{31}$ (TBBT = tert-butylbenzenethiolate) and ultrathin Au-Pd nanocrystals at the same potential.[61,62] Additionally, the partial current density of ~ 45 mA/cm^2 at -1.0 V is about 33-90 % higher than the reported values for Au NP, Mo-doped Au NP, and Au NP containing CeO_x interface.[63-65]." The papers labeled 60-65 in this passage are included in the Reference section of the revised manuscript.

We express our gratitude to the reviewer for thoroughly looking at the manuscript and for the specific comments that strengthen the quality of the review paper. Hopefully, we were able to fully respond to all the valuable comments. We thank you again for considering this paper for publication in *Catalysts.* Should you need more information, please do not hesitate to contact us.