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### Authors

Brown, Levi  
Zang, Wenjie  
Chen, Zejie  
[et al.](#)

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Meeting-report

# Probing Charge Transfer across Various Metal Support Interactions in Heterogeneous Catalysts via 4D-STEM Techniques

Levi Brown<sup>1</sup>, Wenjie Zang<sup>2</sup>, Zejie Chen<sup>3</sup>, Shane Ardo<sup>2,3,4</sup>, and Xiaoqing Pan<sup>1,2</sup>

<sup>1</sup>Department of Physics and Astronomy, University of California, Irvine, CA, USA

<sup>2</sup>Department of Materials Science and Engineering, University of California, Irvine, CA, USA

<sup>3</sup>Department of Chemistry, University of California, Irvine, CA, USA

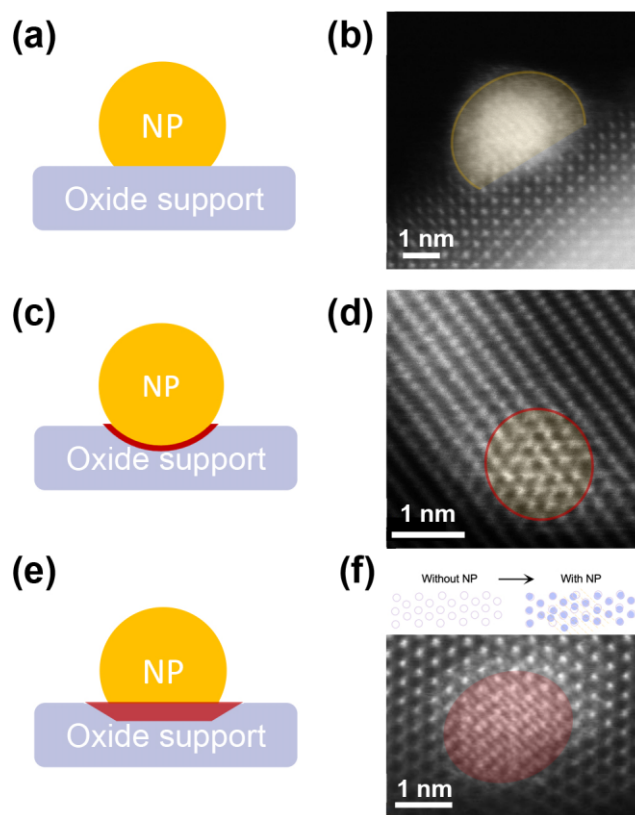
<sup>4</sup>Department of Chemical and Biomolecular Engineering, University of California, Irvine, CA, USA

\*Corresponding author: [xiaoqinp@uci.edu](mailto:xiaoqinp@uci.edu)

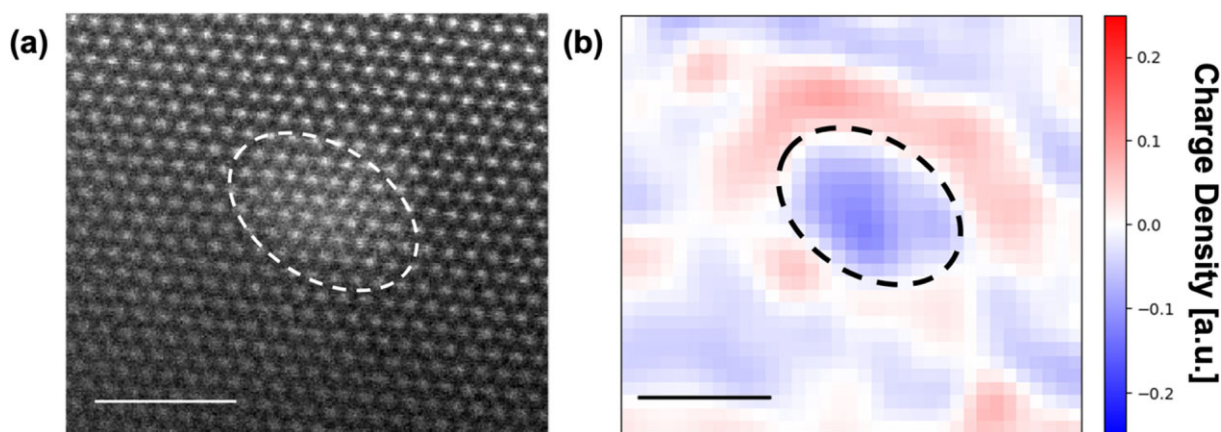
Electronic interactions between metal nanoparticles and their supporting materials are pivotal in determining the functionality of heterogeneous catalysts, affecting their reactivity, selectivity, and stability. In the synthesis of these catalysts, up to twelve distinct metal-support interaction (MSI) types may arise. These interactions, characterized by varying levels of charge transfer and electronic interplay between the metal nanoparticles and their supports, act as crucial tuning levers for enhancing catalytic efficiency [1]. Although photoemission spectroscopy has been employed to study MSIs, it falls short by offering only a generalized view, overlooking the nuanced spectrum of MSIs within a single specimen. The specific charge transfer dynamics surrounding individual nanoparticles are seldom explored [2], leaving the link between charge distribution and catalytic efficacy ambiguous. Therefore, the direct investigation of charge transfer in singular nanoparticles and its impact on catalytic performance remains a significant challenge.

In this study, three types of MSIs were fabricated in the Pt/SrTiO<sub>3</sub> system using a photochemical deposition method from soluble Pt ion precursors over varied illumination durations. Using aberration correct high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM), various MSIs between the SrTiO<sub>3</sub> supports and Pt nanoparticles were surveyed to reveal their degree of incorporation. Short duration exposure yielded “surface adsorption” type MSIs (Figure 1a-b), wherein the nanoparticle was adsorbed onto the support with no visible atomic displacement at the MSI interface. Longer duration exposure yielded the “formation of interfacial interphases” in the MSIs (Figure 1c-d), where the atoms at the interphase region were displaced. Extended duration exposure resulted in the atomic structure of the support deforming and rearranging around the nanoparticle while the nanoparticle’s atomic lattice kept its structure in a type of MSI called “support deformation (Figure 1e-f).” To study the electronic behavior associated with the different MSI formations, we implemented 4D-STEM to map charge density across single nanoparticles. The charge density was calculated by taking the divergence of the inverse shift in the center of mass of each diffraction pattern. By using this method alongside applying a gaussian filter to the image, we were able to clearly visualize the negative charge concentrated on the nanoparticle and the positive charge on the surrounding support of surface adsorption type MSI (Figure 2a-b). Additionally, our recent study confirms that the formation of diverse MSIs have also endowed Pt/SrTiO<sub>3</sub> catalysts with varying efficiency for photocatalytic hydrogen evolution.

In conclusion, we have successfully synthesized several different types of MSIs in heterogeneous photocatalysts and directly observed the morphology and charge density of individual MSIs to characterize the relationship between MSI systems and catalytic performance. The comprehensive methodology of this study yields valuable insights into the role of charge transfer in photocatalyst performance, ultimately facilitating the development of the next generation of highly reactive heterogeneous catalysts [3].



**Fig. 1.** Schematic and corresponding HAADF-STEM images of three MSI types. (a-b) surface adsorption, (c-d) formation of interfacial interphases, and (e-f) support deformation.



**Fig. 2.** (a) HAADF-STEM image of a single surface adsorption MSI and (b) the corresponding charge density map. Negative charge is concentrated on the nanoparticle while perimeter is surrounded by positive charge. The dashed line indicates the perimeter of the nanoparticle. Scalebars are 2nm.

## References

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