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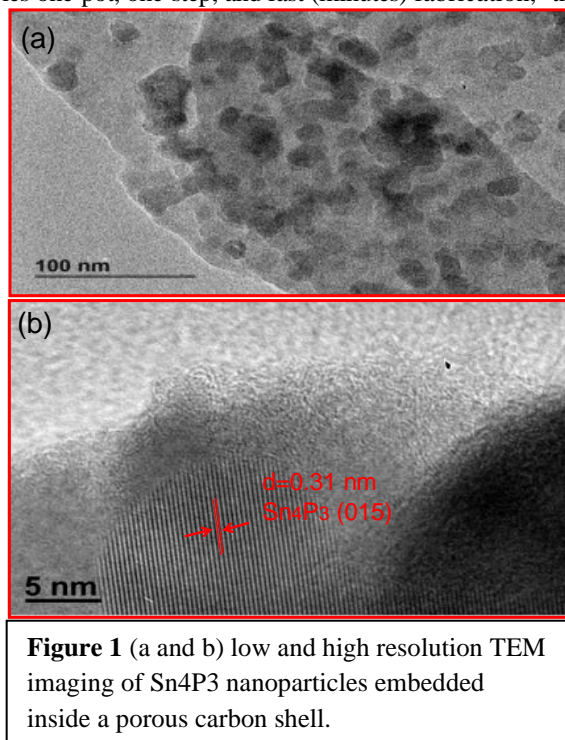
Project Title: Improving Hydrogenation via Anionic Tuning of the Electronic Structures of Transition Metal Compounds

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Progress and ongoing Research:

The main focus in the first grant year is to establish methods for controlled fabrication of transition metal nanostructures with controlled anionic doping their structural characterization. An extremely simple, rapid (minutes) approach for the fabrication of various transition metal phosphide nanoparticle/porous carbon hybrids with a unique nano-architecture. The new approach apply microwave irradiation instead of traditional convection heating for time and energy consumption efficiency. Furthermore, this approach enables one-pot, one-step, and fast (minutes) fabrication, the entire process can be performed under conditions without requirement of protection via an inert environment, either a reductive environment (H_2), which makes this approach even more cost-effective and convenient. With slight adjustment of the microwave irradiation period, this approach can be used to fabricate broad range of metal phosphide nanoparticles, from transition metal, such as Ni, Fe, Co, Pd, to P block elements, such as Sn. Most importantly, thus produced metal phosphide/C hybrid has a very unique nanoarchitecture, in which metal phosphide nanoparticles are encaged by a porous carbon shell instead of being simply immobilized on the surface of a carbon materials. The phosphorus anionic doping, is expected to play weak ligand effect, largely keeps the catalytic activity of the metal centers. While the geometric effect, the “ensemble effect” of P will largely decrease the coke formation, which would causes catalyst deactivation. Further, the outer porous carbon shell would allow full access of the catalytic centers, while further demote coke formation. The catalytic performance and stability of these unique catalysts will be studied soon.



In a joint experimental and computational study, we studied how phosphorus doping could fine tune the surface structure and electronic properties of γ -Al₂O₃ nanoparticles.[1] We found that the electronic properties of metal oxide surfaces can be manipulated via anionic doping (P atoms in this work). The surfaces can be made electron-rich in the sense that they have a lower work function than the undoped ones. The main reason for the work function lowering is the introduction of a surface dipole after doping. Interestingly, we find that the OH groups of thermodynamically stable mono- and bi-dentate Phosphate surface ligands cooperate with the surface by damping its dipole thereby decreasing the work function. Substitutional P-doping leads to nonsymmetric arrangements of P (tri- and four-coordinated) with an added dipole that once again dampens the work functions. The reduced coordination of the P atom correlates with the reported higher catalytic activity of P-doped alumina surfaces. With this study, we paved the way to using group 5A doping as a tuning knob for engineering electrostatic properties of metal oxide surfaces with catalytic applications. This work has results in a joint publication. [1]

Impact on Student Researchers

During the first grant year, two Ph. D students have been supported by this research grant. One of them has been working in developing microwave enabled rapid fabrication approaches for transition metal phosphide nanoparticle for catalytic applications, gaining hands on experience on nanomaterials fabrication and characterization, especially in single nanoparticle level surface work function measurements. The other graduate student got extensive training on high resolution imaging tools, including both high resolution transmission electron microscope

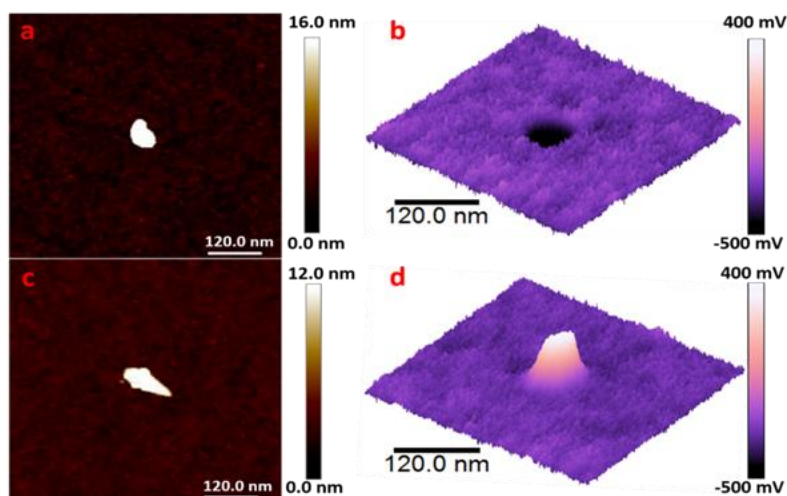


Figure 2 (a and c) Topography and (b and d) potential mapping images of γ -Al₂O₃ and P- γ -Al₂O₃, respectively.

(TEM) and the state-of-the-art scanning transmission electron microscope (STEM), and single atom electron energy loss spectroscopy (EELS) with world leading energy resolution recently developed at Rutgers. Figure 4 shows an image of atomic resolution of graphene surface with a single oxygen atom on the edge of the graphene sheet can be clearly seen. With all these characterization technology handy, we will systemically study the electronic and geometrical confinement of the catalytic centers at the atomic levels, and establish structure-property-function relationship of the series anionic doped transition metal catalysts in the current grant year. This project also enabled one undergraduate to participate research to achieve 9.0 hours of course credit toward his BS degree. This student also presented as an oral presentation at the 67th annual undergraduate research symposium at Queens College in May 2019, won an excellent achievement award. The project also provided opportunity for a minority high school student supported by ACS SEED to gain hands on research experience during this summer. Combined with the knowledge he learned out of his classroom ignited his passion in science, particularly in chemistry.

Future Work

The catalytic performance of the fabricated nanomaterials will be systematically studied in the current grant year. More importantly, we will make full use of the state-of-the-art scanning transmission electron microscope (STEM), and single atom electron energy loss spectroscopy (EELS) with world leading energy resolution recently developed at Rutgers, to systematically study the electronic and geometrical confinement of the catalytic centers at the atomic levels, aiming to understand how the anionic doping could fine tune the electronic structures of the catalytic centers in the transition metal catalysts and establish structure-property and function relationship.

References

- [1] Acikgoz, M.; Khoshi, M. R.; Harrell, J.; Genova, A.; Chawla, R.; He, H.; Pavanello, M., Tuning the electronic properties of the γ -Al₂O₃ surface by phosphorus doping. *Physical Chemistry Chemical Physics* **2019**, *21* (27), 15080-15088.