LOCAL STRUCTURAL STUDIES OF PD-BASED CATALYTIC NANO-PARTICLES

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ABSTRACT

The purpose of this experiment was to focus on the study of the atomic organization of nanoparticles of palladium, palladium/copper, palladium/cobalt, and palladium/nickel. The nanoparticles' structure is studied using Extended X-ray absorption fine structure (EXAFS). X-ray absorption spectroscopy measurements are performed on both edges of the nanoparticles. This allows us to determine the arrangement of the metals within the nanoparticle

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MOTIVATION

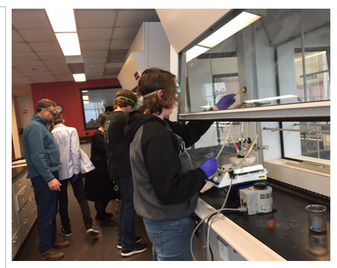
Due to their reduction in size and increase in surface area, bi-metallic nanoparticles (BNPs) are prominently used as catalysts. BNPs have proven to be the best performing catalysts for fuel cell oxidation processes. One of the major problems in understanding how these nanoparticles function is to have a clear picture of their structure. X-ray absorption spectroscopy provides local structural information, which can be used to distinguish core-shell atomic distributions from uniformly alloyed distributions. This kind of structural understanding, combined with the catalytic properties, can help design better catalysts for the future.

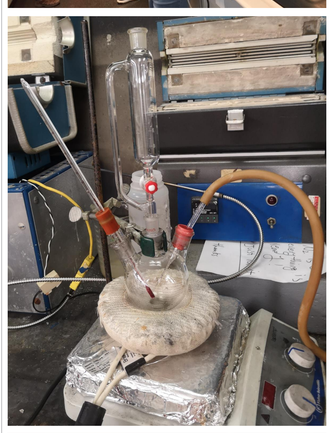
METHODS
Bimetallic Nanoparticle (BNP) Synthesis

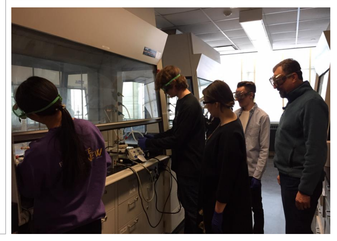
- Nanoparticles of Pd and BNP, Pd_3Co, Pd_3Cu, Pd_3Ni were synthesized on Graphene Oxide (GO) flakes at IIT in the chemistry laboratory using the following reaction (for Pd_3Co):

  $3\ PdCl_2 + CoCl_2 + 4\ NaBH_4 \Rightarrow Pd_3Co + 4\ BH_3 + 4\ NaCl + 4\ HCl$

- Pd salt measured in a 20 ml beaker dissolved with 10 ml acetone and GO flakes
- Transition metal measured in 20 ml beaker dissolved in DI water
- Transition metal solution placed in round bottom flask and stirred for 3-5 min, Pd/acetone solution is then added
- Stir solution as temperature rises toward 80°C
- Measure 10x of $NaBH_4$ dissolve in 20 ml of DI water
- When Pd/Co solution reaches 80°C, add $NaBH_4$, and terminate reaction by stopping heat while continuing to stir
- Once cooled to room temperature, filter precipitate under vacuum using PEM filter, dry in oven after rinsing and filtering several times



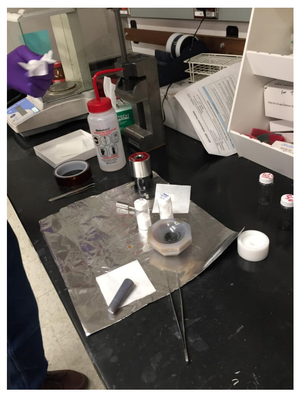


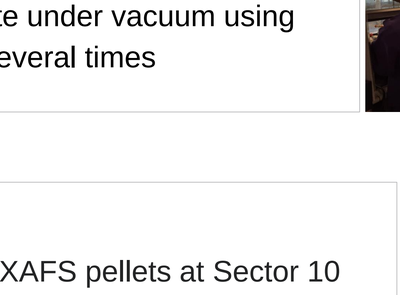


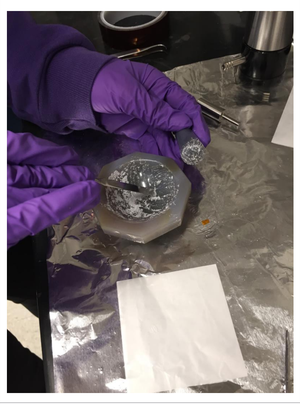
METHODS - EXAFS Samples

The BNPs were then formed into transmission EXAFS pellets at Sector 10 (MR-CAT).

- Using the model edge jump calculation spreadsheet calculate the amount of sample required to get approximately an edge jump of 1.
- Weigh out appropriate amount of sample
- Add a medium spatula full of boron nitride (BN)
- Add a spatula tip of PVDF (polyvinylidene difluoride) as a binder
- Grind in mortar and pestle, scraping powders down to the bottom of the mortar several times until color is uniform
- Pour powder into the pellet die, press in vise to hand tight
- Flip pellet die over and push sample out from the bottom and wrap pellet in thinnest Kapton tape available





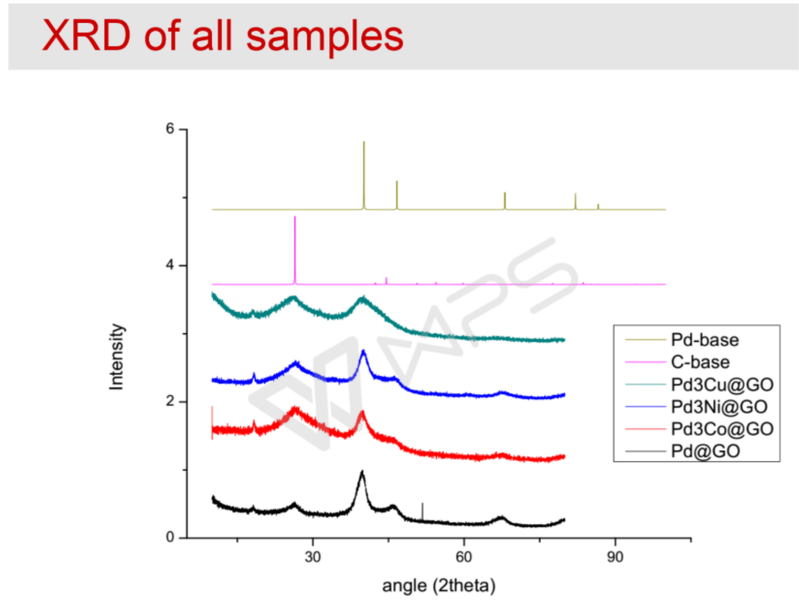


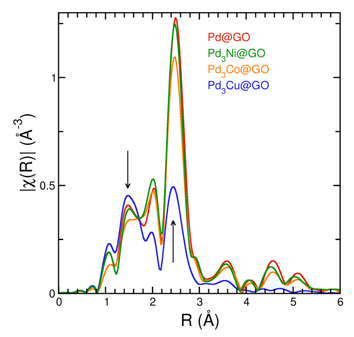
DATA

Table 1 : Results of the XRD fitting, showing particle sizes in Angstroms and lattice parameters

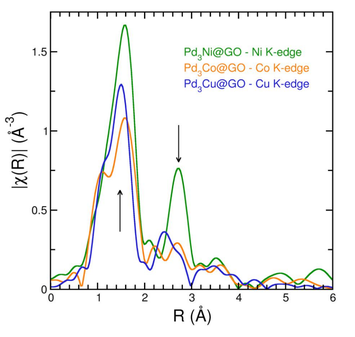
	Lattice parameter – a (Å)	Nanoparticle diameter – d (Å)
Pd@GO	3.934	38
Pd_3Cu@GO	4.040	20
Pd_3Co@GO	3.952	38
Pd_3Ni@GO	3.929	40

The figure below shows the graphs of the XRD results; as shown, it is evident that the Pd and 3d metals are located in the same areas, so that they are not segregated in different nanoparticles.





Graph 1: This graph shows the EXAFS for the Pd from each sample. The upwards-pointing arrow indicates the Pd-Pd bond. The downwards-pointing arrow indicates the Pd-O bond.



Graph 2 : This graph shows the EXAFS of the 3d transition metals for each of the three compounds. The upwards-pointing arrow indicates the M-O bond. The downwards-pointing arrow shows the M-Mi/Pd distance.

CONCLUSIONS

- It appears that the palladium metal (Pd) is at the core of the nanoparticles created, while the Cu, Ni, and Co have oxidized, placing them near the edge of the nanoparticles.

NEXT STEPS

- Further investigation of the mixing of elements inside of the metallic core would reveal new information that could lead to innovations in the production of fuel cells and possibly in other fields.

REFERENCES

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