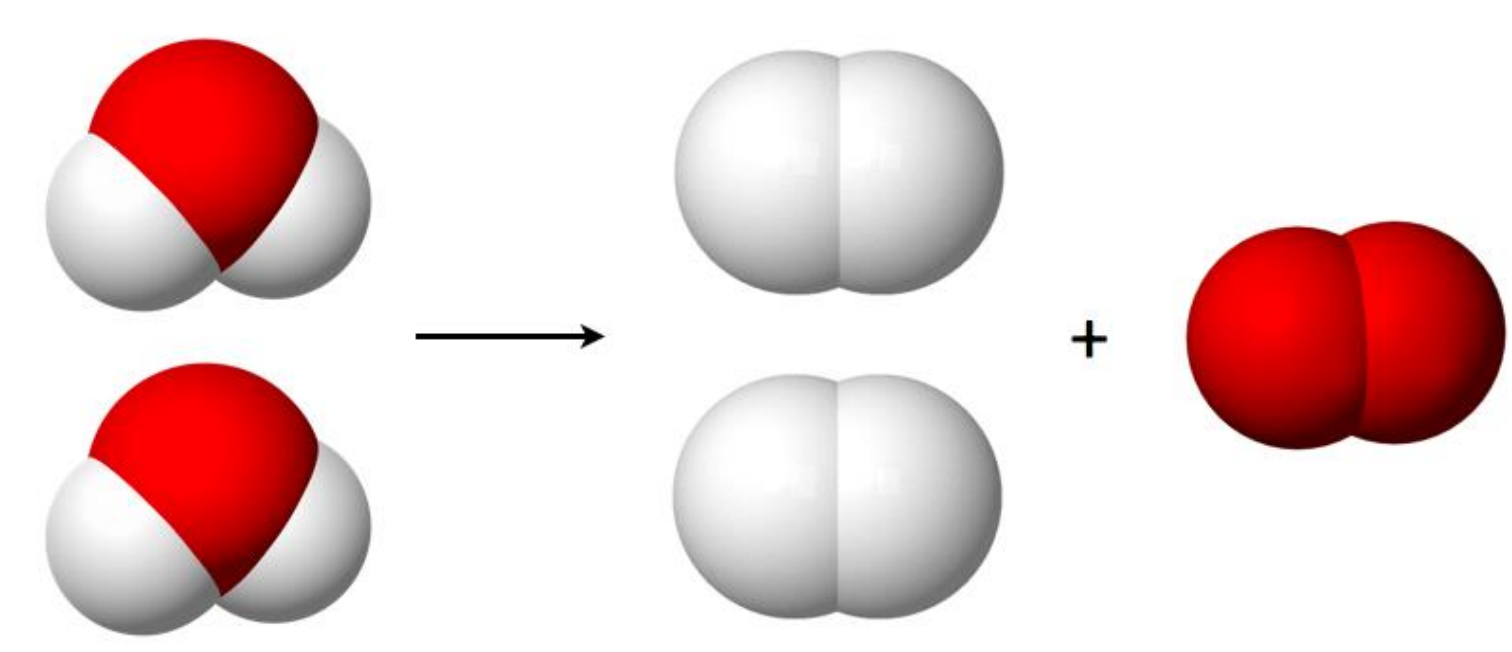


Olivia Bennett¹, Matthew Hershey², Dr. Dayne F. Swearer^{2,3}¹Tufts University, ²Northwestern University Department of Chemistry, ³Northwestern University Department of Chemical and Biological Engineering

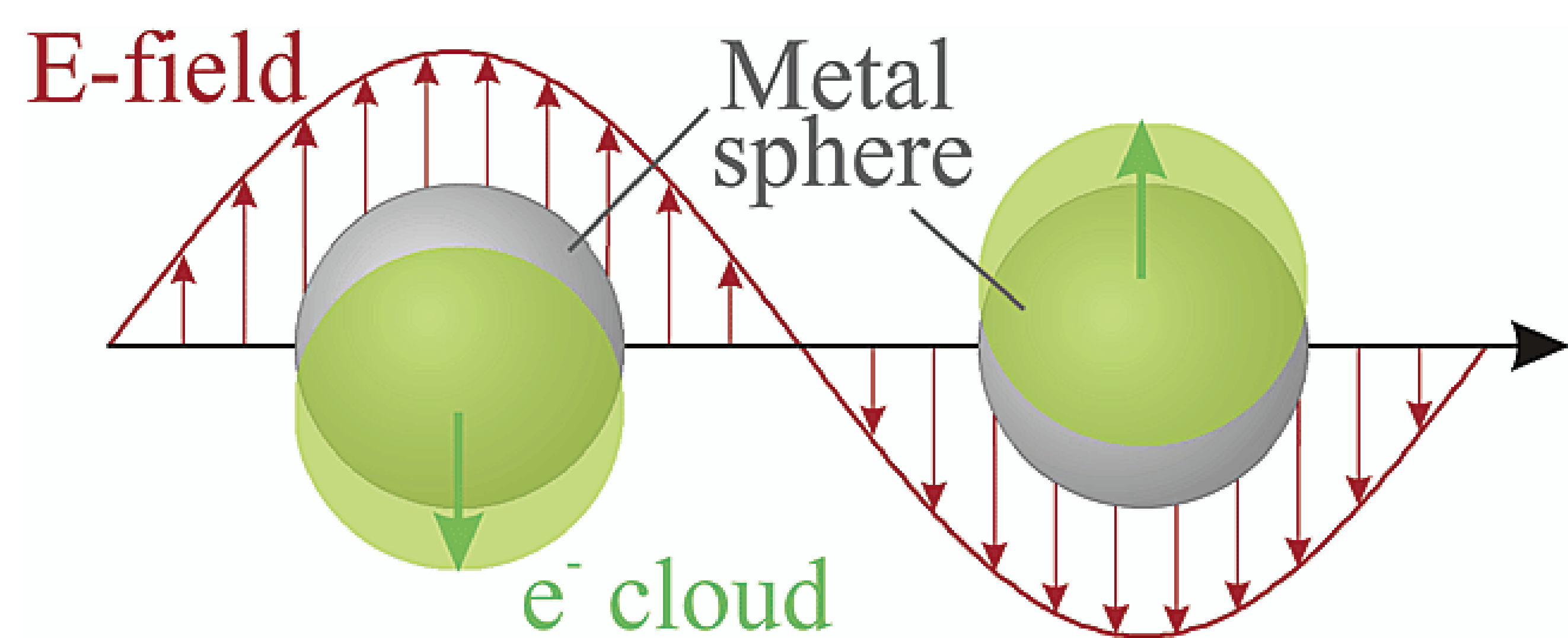
Abstract

Current industrial catalytic processes are highly energy intensive, requiring extreme temperatures to overcome the thermodynamic and kinetic thresholds of the reaction. Presently, this energy comes from the combustion of fossil fuels. Utilizing the localized surface plasmon resonance (LSPR) effects present in plasmonic metal nanoparticles, light can provide the necessary energy instead, lowering the overall energy draw. Plasmonic aluminum nanoparticles coated with catalytic metal oxides were produced via colloidal synthesis. Optical activity, conformational, and compositional data were characterized using UV-visible spectroscopy (UV-vis), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). These plasmonic-core catalytic-shell nanoparticles can be employed as photocatalysts for industrial chemical processes.

Background

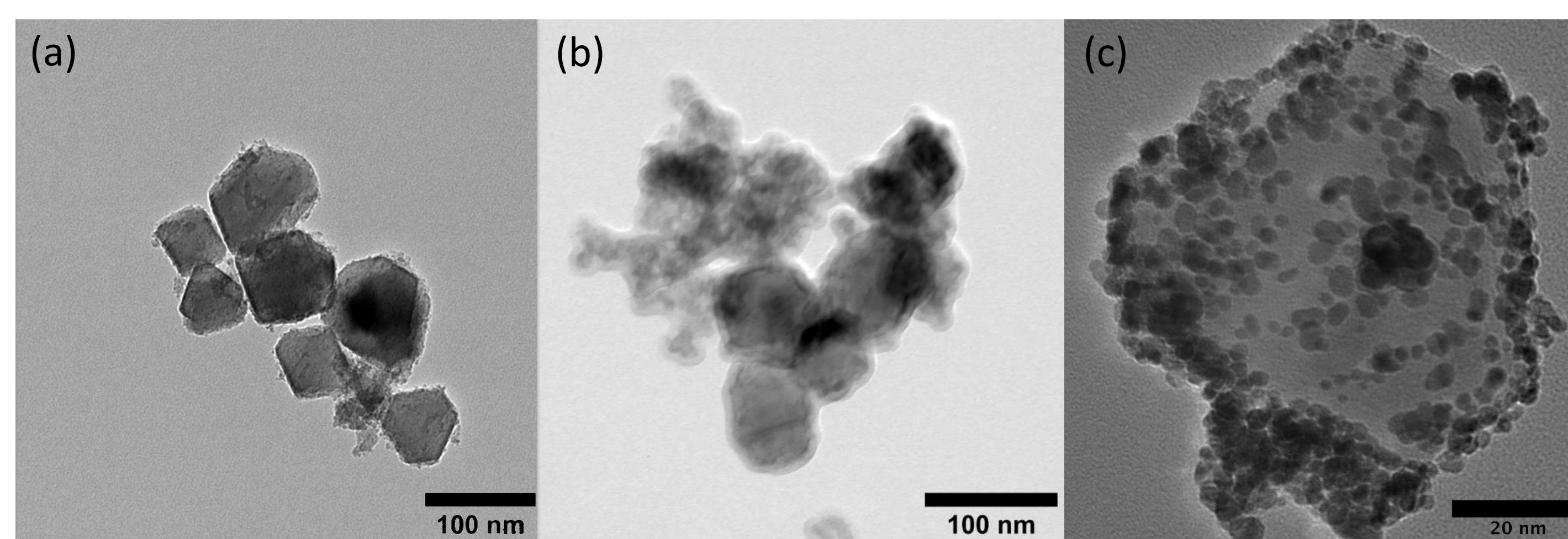
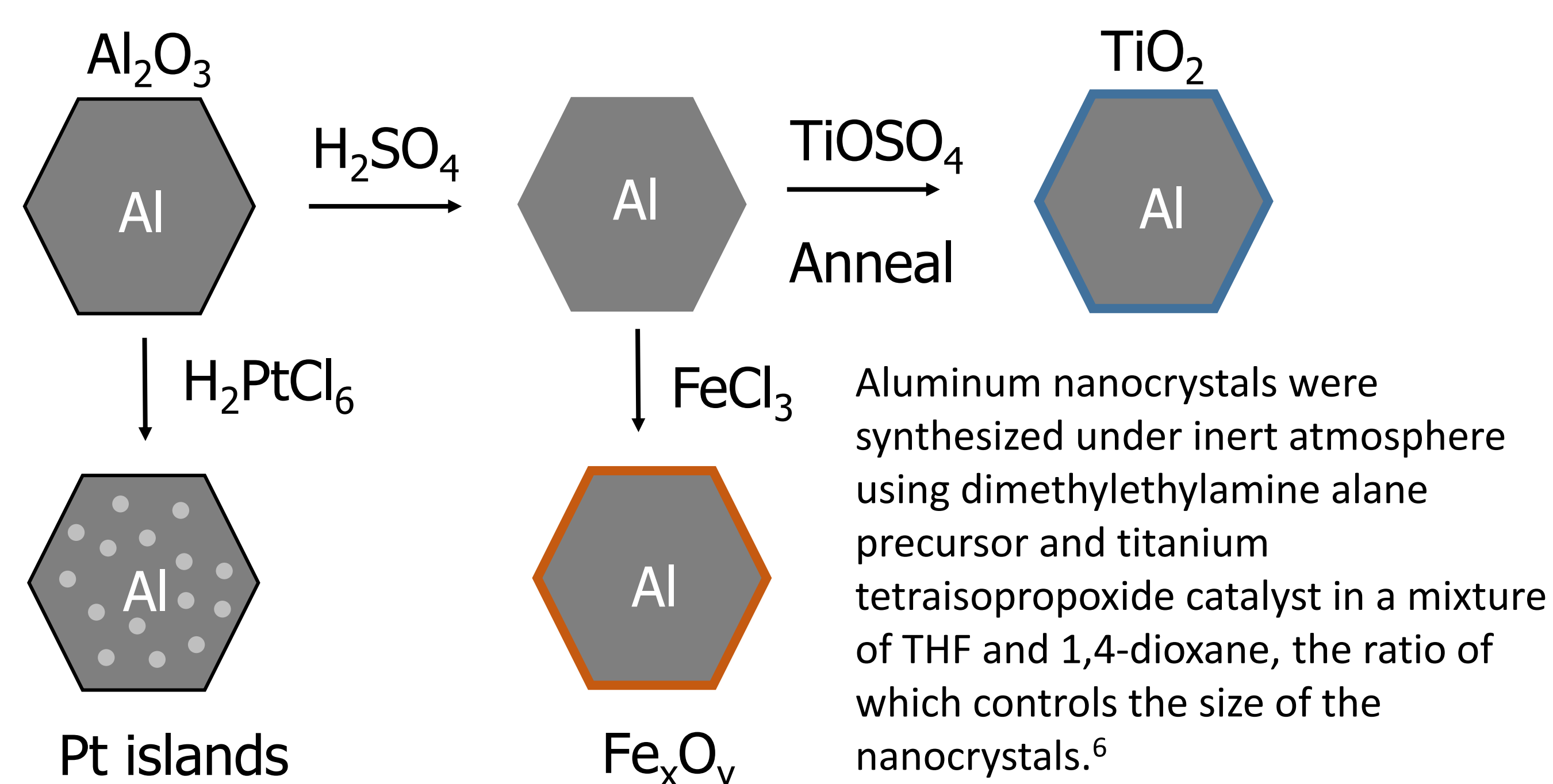
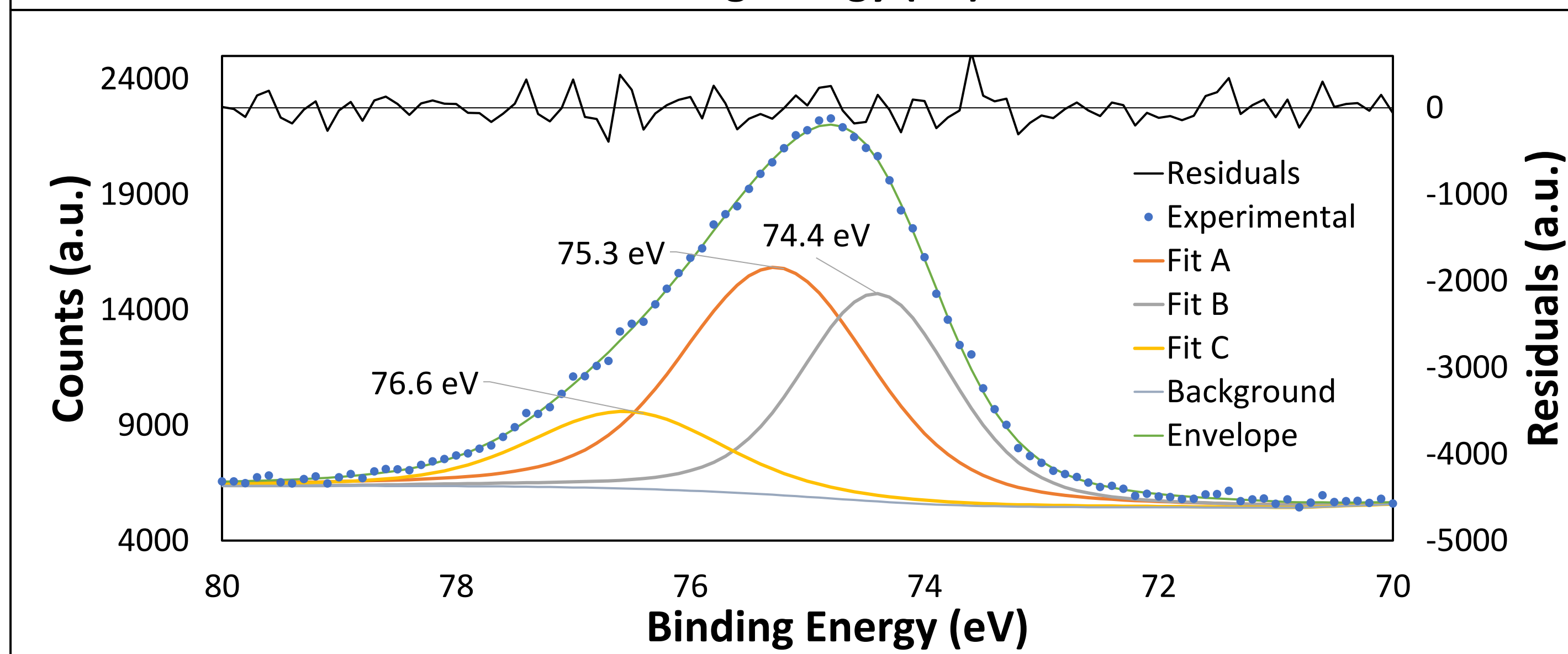
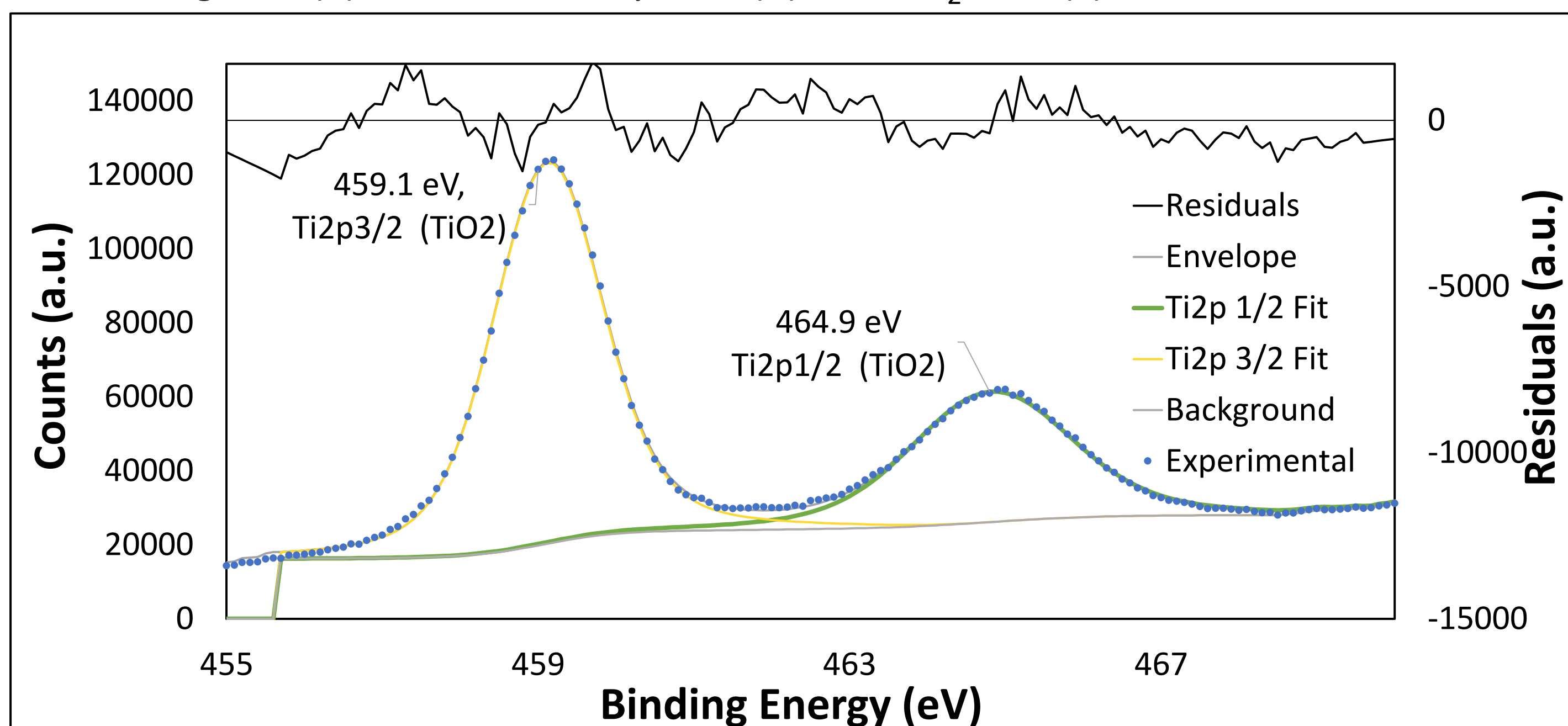
Schematic of the water splitting reaction.¹Thermocatalysis \rightarrow Photocatalysis

The water splitting reaction is a potential carbon-free source of hydrogen. This energy intensive process currently relies on electricity. Developing a photocatalyst for this reaction may reduce the electricity draw and revolutionize the production of hydrogen on the industrial scale.

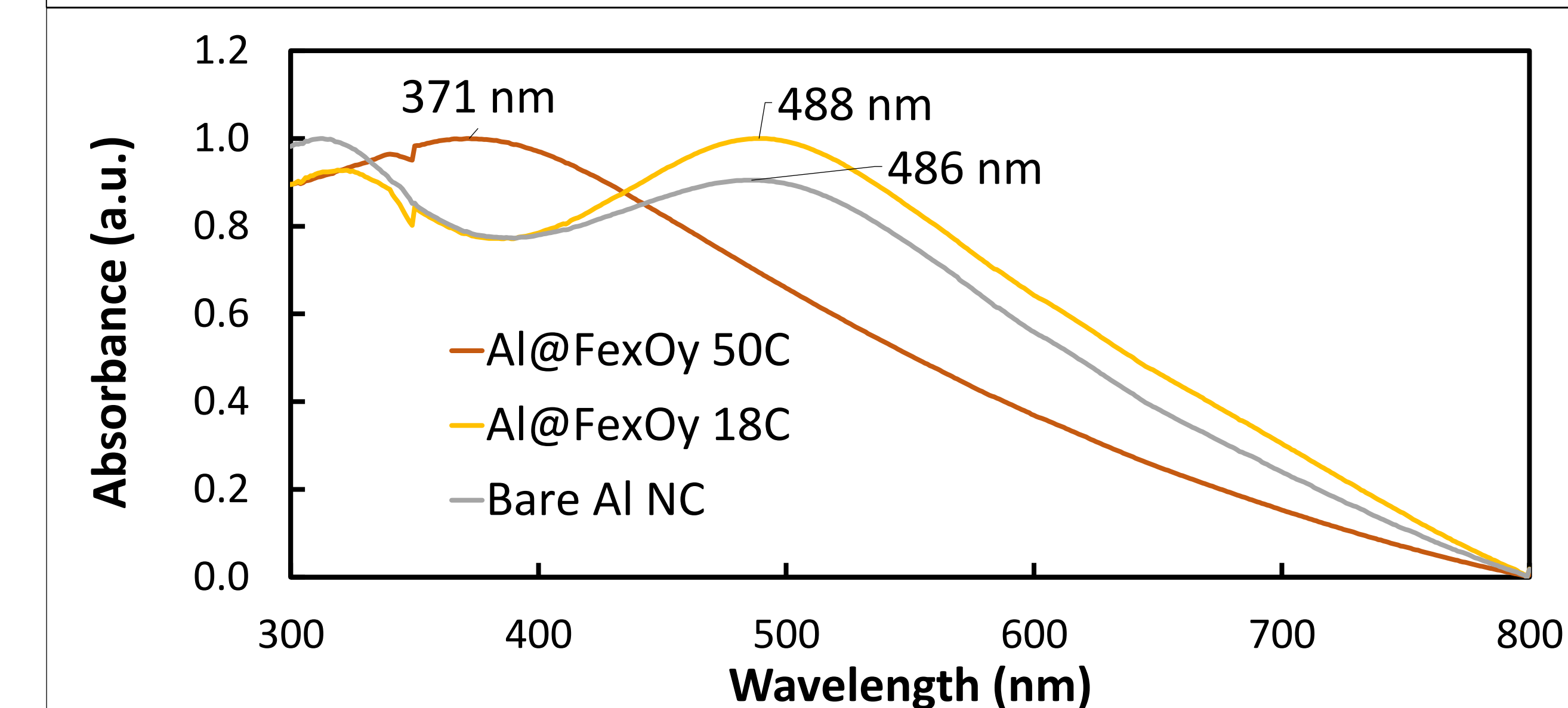
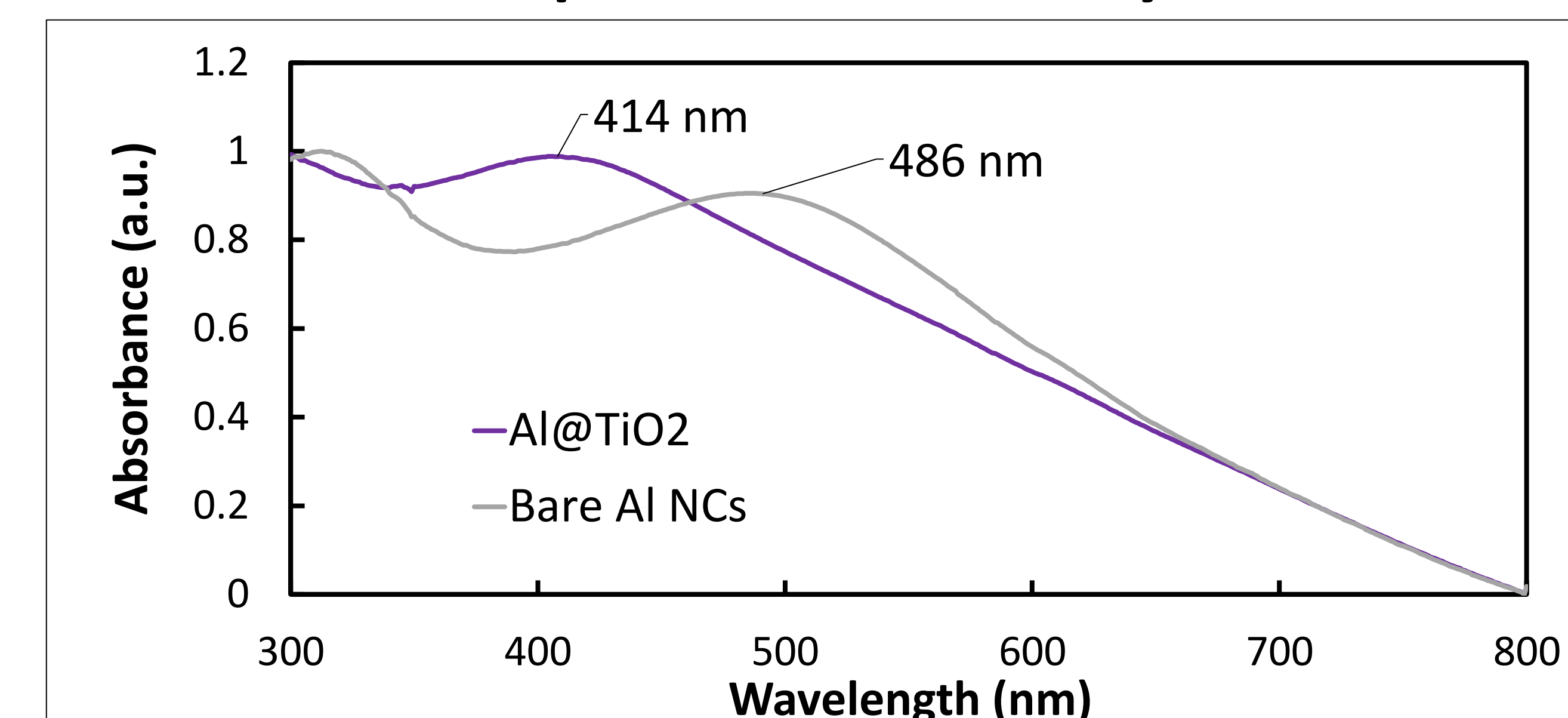


A collective electron cloud oscillation is known as a plasmon, and the frequency at which this occurs called the localized surface plasmonic resonance (LSPR). This phenomenon causes plasmonic nanoparticles to have unique optical properties that can be utilized for catalysis.^{2,3} When a plasmonic core is combined with a catalytic coating, the LSPR can inject energy from the plasmon into the coating, providing the energy necessary to drive the reaction.⁴

Synthesis and Characterization

TEM images of (a) bare Al nanocrystals, (b) Al@TiO₂, and (c) Al@PtXPS spectra confirming the presence of TiO₂ (top) and aluminum (bottom).

Optical Activity



Conclusions and Future Work

Experiments assessing the photocatalytic activity of these particles should be performed to gain insight to their activity, selectivity, and stability. Future studies of these materials should examine the ideal particle size and shell thickness, as well as investigate the catalytic properties of these particles. Techniques such as online mass spectrometry, modulated-excitation Fourier transform infrared spectroscopy, and ultrafast electron microscopy may be employed to accomplish this goal.

References and Acknowledgements

This research was supported primarily by the International Institute for Nanotechnology's Research Experience for Undergraduates Program under the National Science Foundation award numbers EEC-1757618. Any opinions, findings, conclusions, or recommendations expressed in this material are those of the authors and do not necessarily reflect those of the NSF. Thank you to Dr. Dayne Swearer, Matt Hershey, Emma-Rose Newmeyer, Jamie North, Javier Cabezas Parra, Benjamin Hirschboeck, and Kyle Hur for their daily support.

- Water Splitting. *Wikipedia*. Accessed 8 Aug. 2022
- Boken, J.; Khurana, P.; Thatai, S.; Kumar, D.; Prasad, S., Plasmonic nanoparticles and their analytical applications: A review. *Applied Spectroscopy Reviews* 2017, 52 (9), 774-820.
- Kelly, K. L.; Coronado, E.; Zhao, L. L.; Schatz, G. C., The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment. *The Journal of Physical Chemistry B* 2003, 107 (3), 668-677.
- Bayles, A.; Tian, S.; Zhou, J.; Yuan, L.; Yuan, Y.; Jacobson, C. R.; Farr, C.; Zhang, M.; Swearer, D. F.; Solti, D.; Lou, M.; Everitt, H. O.; Nordlander, P.; Halas, N. J., Al@TiO₂ Core-Shell Nanoparticles for Plasmonic Photocatalysis. *ACS Nano* 2022, 16 (4), 5839-5850.
- Jang, J.-W.; Du, C.; Ye, Y.; Lin, Y.; Yao, X.; Thorne, J.; Liu, E.; McMahon, G.; Zhu, J.; Javey, A.; Guo, J.; Wang, D., Enabling unassisted solar water splitting by iron oxide and silicon. *Nature Communications* 2015, 6 (1), 7447.
- Clark, B. D.; DeSantis, C. J.; Wu, G.; Renard, D.; McClain, M. J.; Bursi, L.; Tsai, A.-L.; Nordlander, P.; Halas, N. J., Ligand-Dependent Colloidal Stability Controls the Growth of Aluminum Nanocrystals. *Journal of the American Chemical Society* 2019, 141 (4), 1716-1724.
- Swearer, D. F.; Leary, R. K.; Newell, R.; Yazdi, S.; Robotjazi, H.; Zhang, Y.; Renard, D.; Nordlander, P.; Midgley, P. A.; Halas, N. J.; Ringe, E., Transition-Metal Decorated Aluminum Nanocrystals. *ACS Nano* 2017, 11 (10), 10281-10289.