

The Power of Hydrogen

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Hello, my name is Sumit Bawari, and what follows is the story of my encounter with a rather tedious assemblage of materials and their catalytic property. Dear reader, what I am writing may not be exactly in the scientific frame of mind. But I shall try to convey my experience during this study. Since people at AWSAR have been rather liberal with the maximum word count, I shall provide a background as well.

My host institution is the newly operational campus of the Tata Institute of Fundamental Research (TIFR), located in the outskirts of the city of Hyderabad. In the year 2015, I joined the integrated PhD course here in chemistry. Mingled with the fear of being so far away from home, and the excitement of trying out new things, I braced for the journey that would be my PhD. But before actually registering for PhD, one has to complete coursework. As opposed to traditional MSc courses, the I-PhD course gives more weightage to one's research projects rather than coursework.

While I barely skimmed by in courses, the projects were something I had never encountered before. Me, a mediocre BSc student from the University of Delhi, who had never experienced the gentle touch of a micropipette, had never plotted my own data, and never known what research papers were. And while fellow students went for summer projects, I went home to relax in the hills of my homeland Uttarakhand. Please do not mind the digression dear reader, but one has to sidestep once in a while, to grasp the whole story.

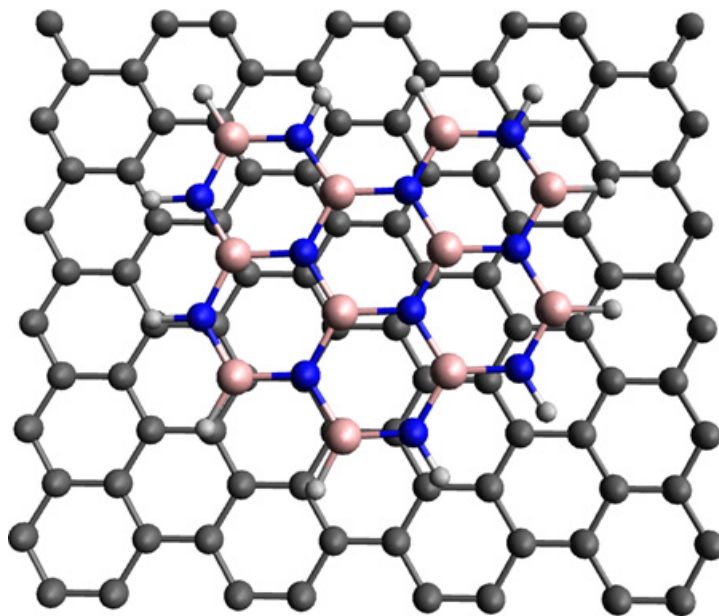
Anyway, finally in the fourth paragraph, I will talk to you about my project. I chose Dr. T. N. Narayanan (TNN), who is a material scientist as my project guide. Joining his team reminds me

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of a funny thing he said, when I was leaving for home on vacation before the project. I had asked him to give me material to read while at home. He just smiled and said, “We will discuss when you come back, it’s not like you’re going to read it anyway.” I just nodded, smiled and walked away; thinking he probably remembers being a student himself.

When I came back, I started work on chemically coupling graphene sheets. I’m certain the reader must be familiar with the structure of graphite (if not there’s always Google). Graphene is a single sheet of hexagons of carbon forming large sturdy sheets. For perspective, if you draw a faint line with your graphite pencil, you will form layers that have 100-1000s of layers of graphene. Graphene has often been called the “wonder material” by many, as has the potential to replace and improve most modern technologies. In our case, we focus on graphene for catalysis, due to its overwhelming surface area.

Shubhadeep had already found the method promising in coupling carbon nanotubes, which are just rolled up graphene sheets. Predicting enhanced catalytic properties, we started the tiresome coupling process. The coupled sheets came out completely different from the initial dispersed



oxidized graphene sheets. They had formed clumps where some were floating to the top, while some were settling on the bottom. Intrigued by their weird behaviour, we made inks of the same and began catalysis experiments.

Electrocatalysis is the conversion of electrical energy into chemical energy. Specifically, our reaction of study is abbreviated as HER (Hydrogen Evolution Reaction). This particular reaction can, in simple terms, break water to form hydrogen. Hydrogen, believed to be the fuel of the future, requires a way of efficient hydrogen production. Till now, only a handful of hydrogen powered cars and trains are operational. And to make this hydrogen powered future a reality, scientists have to

develop cheaper and efficient catalysts. The reader should realize the benefit of powering their cars just by using their pencils.

Anyway, it turned out that even though the same coupling for CNTs gave promising hydrogen production activity, our grapheme based sheets did not. This result was more intriguing than disappointing, and reflected on our lack of knowledge of the system. After this initial failure, we tried something planned yet outrageous. This time, during the coupling reaction we added, along with everything else, small amounts of hexagonal Boron Nitride (hBN). Hexagonal Boron Nitride can be thought of as analogous to graphene where instead of carbons everywhere, one finds alternating borons and nitrogens. The interaction of graphene with hBN is well known and our advisor was probably playing at that. Surprisingly, graphene-hBN composites had tremendous hydrogen production activity. Slightly better than coupled CNTs, but lagging behind platinum. This promising result came with its own questions, as to what was the cause of this activity.

This marked the end of my first project. For my second project, I aimed at learning computational simulations. And the only person, at that time, whose work involved computation in chemistry was Dr. Jagannath Mondal (JM). And it so seemed that TNN and JM had already conspired behind my back, and I was to continue studying the graphene-hBN hydrogen evolution activity, now from the simulation point of view. For better or worse, JM worked on biomolecules and had never actually worked on materials. And while most of the catalytic materials community relied on DFT (Density Functional Theory) calculations, JM did molecular dynamics (MD). Due to this, we were forced to look at the bond breaking problem in a form where bonds cannot break.

After some literature and soul searching, we decided on studying specific steps in the reaction, for a reaction to occur the reactant has to get there first. And the product also needs to get away, so that it doesn't overcrowd the place. We studied water ion adsorption and hydrogen desorption on our graphene-hBN picture, and found that the hBN edge can selectively adsorb water ions and also desorb hydrogen, when the hBN is stacked on graphene. This phenomenon provided some explanation for the unexpected improvement of catalytic activity, but JM and TNN were not still not satisfied.

Then came the time for my third and final project before I could register for a PhD. This turned out to be another collaboration between JM and TNN, where I had to helplessly shuffle between computation and experiments. Since we had some background proof regarding the hBN effect on graphene, the same had to be tested on a non-coupled environment. Almost pure and slightly oxidized graphene both were studied, and both gave enhanced catalytic hydrogen production when mixed with hBN. For a complete view of the reaction process, JM removed his MD shackles and delved into the DFT realm. This also marks the entry of Nisheal Kaley into the picture, a project student who had some previous DFT knowledge. Together, Nisheal and I, uncovered that the hBN has a polarizing effect on the graphene. And this makes the carbons in graphene active for hydrogen evolution.

Now, after two published and one report in compilation, we know that hBN can adsorb the water ion, make the graphene lattice polarized for bonding steps, and also desorb the product hydrogen, while just sitting on top of graphene. I hope the reader has not been too caught up in jargon, and can appreciate the elegance of stacked heterostructures for catalytic applications.

Publications on the topic:

1. Atomistic Elucidation of Sorption Processes in Hydrogen Evolution Reaction on a van der Waals Heterostructure, Sumit Bawari, T. N. Narayanan, and Jagannath Mondal, *The Journal of Physical Chemistry C* 122 (18), pp 10034–10041 (2018).
2. On the Hydrogen Evolution Reaction Activity of Graphene hBN van der Waals Heterostructures, Sumit Bawari, Nisheal M. Kaley, Shubhadeep Pal, Vineesh T V, Shamasree Ghosh, Jagannath Mondal, and T. N. Narayanan, *Physical Chemistry Chemical Physics* 20, 15007-15014 (2018).