

The Effect of Varying Compositions of AgBr/g-C₃N₄ Nanocatalyst on Catalysis Efficiency of
CO₂ Reduction for Artificial Photosynthesis

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Introduction

Artificial photosynthesis is a process that utilises solar energy to convert atmospheric CO₂ into usable fuels. This is a highly desirable process for combating climate change as it not only removes CO₂, a harmful greenhouse gas from the atmosphere, it also reduces the demand for the mining of new fossil fuels. This is increasingly important as the Intergovernmental Panel on Climate Change released a report detailing the necessity for immediate action against climate change and the potential devastating effects if left untreated.^[8]

Artificial photosynthesis is unfortunately majorly inefficient, barely reaching efficiencies of 3% of the solar energy harvested compared to 15%-20% efficiencies of current photovoltaic panels. Then additional energy is lost in the actual utilization (usually combustion) of the products of artificial photosynthesis. The core of artificial photosynthesis is CO₂ reduction, a chemical reaction that reduces the oxidation state of carbon in CO₂, producing a chemical that stores energy to be released later. Oxidation state is a number that provides some additional information about an atom in a molecule. Oxidation state refers to, in a simple sense, how many electrons that atom is sharing with another atom. For CO₂, carbon's oxidation state is +4 because it is sharing 4 of its electrons with the oxygens. For CH₄, carbon's oxidation state is -4 because it is sharing 4 of the hydrogen's electrons. In general, for carbon compounds, the lower the oxidation state, the more energy is stored in that molecule that can be released in combustion later. Since the reduction reaction reduces carbon's oxidation state, energy is being stored in the products.

The reduction reaction requires a catalyst present for the reaction to occur. It is known that the most prominent variable in the efficiency of the overall artificial photosynthesis process

is the ability of the catalyst to reduce the activation energy of the reduction reaction. This is best demonstrated through an analogy. Suppose there is a boulder at the bottom of a hill. The boulder represents the energy of a molecule and the position of the boulder represents the molecule. The bottom of the hill, where the boulder is now, represents CO₂, a very low energy molecule. At the very top of the hill, there is no flat ground and the boulder could not rest there with any stability, representing the lack of a stable molecule at that energy state. Somewhere past the top of the hill, there is a flat spot where the boulder could rest if the boulder were pushed all the way up and over the top of the hill and then kept going to the flat spot. The sun's energy is what gives the boulder a push in this analogy but the pushes are almost never strong enough to get the boulder all the way up and over the hill. This is where the catalyst comes in- the catalytic digs away at the top of the hill so that while the net effect is the same as the boulder would end up in the same flat spot with a sufficient push, it does not have to initially go as high. This allows the boulder to make it to the flat spot more often. The more the catalyst digs down, the more often the boulder can make it and the more efficient the artificial photosynthesis process is.

Literature Review

There are a variety of potential methods for increasing the effectiveness of the catalyst in CO₂ reduction. One method is doping or codoping which shifts the range of light that the catalyst can absorb so it would be like pushing the boulder harder in the earlier analogy. This has proved very effective at raising artificial photosynthesis efficiency but is limited in scope and lacks pathways for improvement.^{[6][7][19][28]} According to Raziq et al. P-B co-doping and SnO₂ coupling improve g-C₃N₄ catalysis by a factor of approximately 8.^[6] This result was one of the

first to attempt codoping with a g-C₃N₄ catalyst base and demonstrated the compatibility.

Another method is cocatalysis or coupling. This adds another catalyst to the original catalyst that further lowers the activation energy of the reaction. It does not simply lower the activation energy because it is another catalyst but it reacts hand in hand with the other catalyst to assist it in how much it can lower the activation energy. Many cocatalysts can be added to keep attempting to lower the activation energy and this is a very active field of research to find the best combinations.^{[19][23][24]} A final method of increasing efficiency is by increasing the surface area of the catalyst, this allows the catalyst to interact with as much CO₂ as possible. This method creates results that, while not insignificant, are very minimal compared to the other methods of increasing efficiency.^{[7][24]} It has been shown that the biggest limiting factor in artificial photosynthesis is the access to sunlight, not CO₂, however, it doesn't hurt to add CO₂.^{[24][29]}

Through the analysis of these sources, it is clear that the gap in research is in cocatalysis and coupling. There are numerous combinations that haven't been tried and by combining these methods with doping and nanoparticle structure, the overall efficiency of artificial photosynthesis could be improved. One specific method that has not been tested is codoping g-C₃N₄ with AgBr nanoparticles. AgBr codoping has, in the past, been a very effective method of increasing efficiency. According to Zhuxing et al., AgBr addition has demonstrated a nearly 10 times increase in efficiency in some cases.^[29] With the multifaceted approach to attacking climate change, as well as the relatively cost efficient design of artificial photosynthesis, it could become viable even with a lower efficiency than current photovoltaic technology.

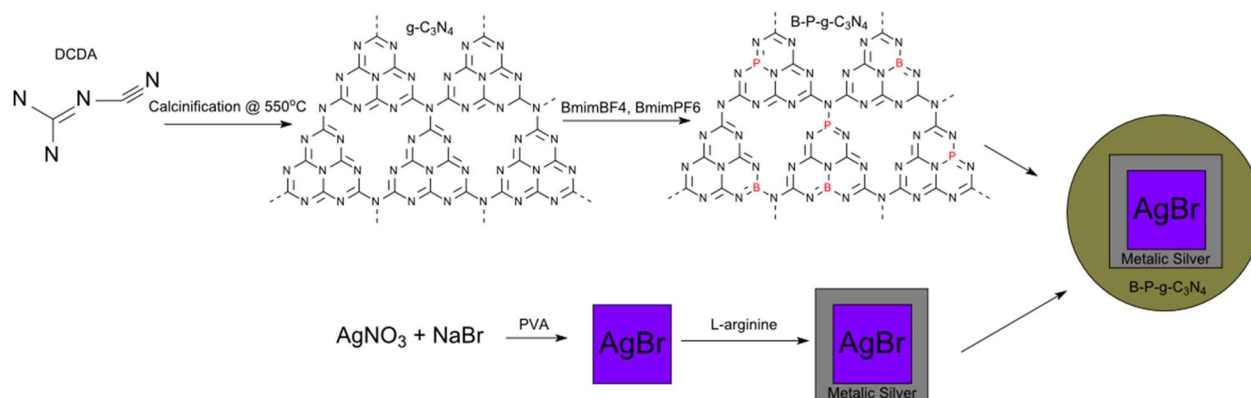


Figure 3 – (Courtesy student) This reaction scheme demonstrates the entire synthesis accomplished by this project.

It shows the process of synthesizing both the g-C₃N₄ and the AgBr nanoparticles and combining them.

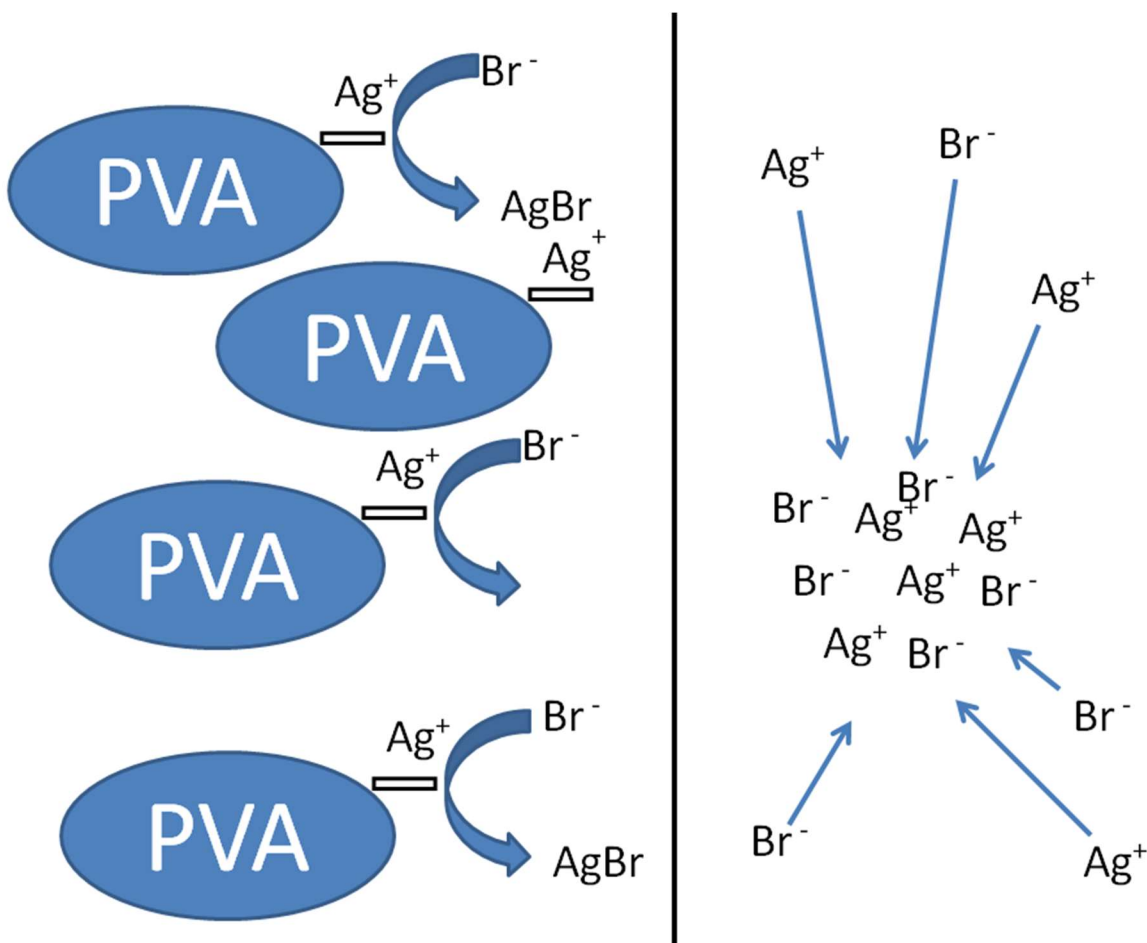


Figure 4 – (Courtesy student) This diagram indicates the importance of including PVA for synthesizing the nanoparticles. While simply mixing AgNO₃ and NaBr would result in AgBr, they would be much too big for this project. The addition of the PVA holds the Ag ions until a Br ion comes close enough to pick it up. This slower process results in much smaller particles because the Ag ions can't rush into a glob, they must be picked up by a Br ion.

Methods

These methods aim to measure the effectiveness of AgBr/B-P-CN with different mass percentages of AgBr in CO₂ reduction for artificial photosynthesis. This was accomplished through synthesizing the catalysts with varying amounts of AgBr nanoparticles, then testing the catalysts under light within a CO₂ atmosphere in aqueous suspension, and finally, analysing the

composition of the atmosphere at certain time intervals. The composition of the atmosphere, particularly the concentration of the products of CO₂ reduction, indicate how efficiently the catalyst converts light stimulation into usable products.

CN Nanosheets

First the g-C₃N₄ (CN) nanosheets were synthesized. This was accomplished through the calcification (heating to decomposition under a select atmosphere) of dicyandiamide (DCDA) under air. 50g of DCDA were heated in a ceramic crucible in a muffle furnace at 550° C for 4h. The material was then cooled to room temperature, ground into a powder using a mortar and pestle, and re-calcined at 550° C for 3h to obtain the CN nanosheets. This method is the most tested and cost effective method of synthesizing CN nanosheets and was chosen for these reasons. (Raziq F., et al., 2017)

B-P-CN Nanosheets

Next, the nanosheets were co-doped with Boron and Phosphorus, achieved using ionic liquids. Ionic liquids are salts that are liquid at room temperature. These are very rare, hard to synthesize, and expensive. This is the only method of doping CN nanosheets that has been successful in the past and unfortunately is quite expensive, limiting the budget for other sections of the method. Additionally, these ionic liquids are the most controlled chemicals that are used in this experiment and consequently have the latest delivery date, increasing time constraints. A certain amount of 1-butyl-3-methyl imidazolium-tetra-fluoroborate (BmimBF₄) and 1-butyl-3-methyl imidazoliumhexafluorophosphate (BmimPF₆) was dissolved into 50 ml of deionized water and stirred for 1h. Subsequently, 4g of DCDA was added to the mixture and it was heated to 100° C until all water had completely evaporated. The resulting white solid was milled and

heated in a ceramic crucible at 350° C for 2h and then the temperature was raised to 550° C at a rate of 5° C/min and held at this temperature for 4 hours. The material was cooled to room temperature and milled and calcined at 550° C for 3h to obtain B-P-CN nanosheets.

AgBr Nanoparticles

Next, the AgBr nanoparticles were synthesized. AgBr has been demonstrated to be one of the most effective cocatalysts for TiO₂ catalysts which is why it was chosen. (Zhuxing, S. et. al., 2018) AgBr has been shown to increase light absorption that will allow the g-C₃N₄ to catalyze more CO₂. Additionally, attaching the g-C₃N₄ to the nanoparticles will increase surface area. This specific method of manufacturing was chosen for its highly controlled particle sizes compared to other methods such as simply combining AgNO₃ and NaBr. AgNO₃ was added to a PVA solution, then a stoichiometric amount of NaBr was added dropwise to the mixture under vigorous stirring. A stoichiometric amount is the amount of a reagent needed to completely consume both reactants if the reaction goes to completion. This isn't always done because most reactions will not go to completion even if a stoichiometric amount of reagents are used and one reagent usually costs more than the others and this is the one that is more desirable to be completely consumed in the reaction and not wasted. In the case of this experiment, the reaction is very favorable (likely to occur) so a stoichiometric amount was used. The reaction proceeded for 30 minutes. Then, L-Arginine was added as a reducing agent and the reaction continued for an additional 45 minutes. A reducing agent is a reagent that is likely to reduce the oxidation state of other molecules in a reaction. This was used to reduce the Ag⁺ ions into metallic (neutral) Ag which coated the nanoparticle. The metallic Ag (silver) partially helps absorb light but mostly helps with transferring the energy absorbed by the nanoparticles into the g-C₃N₄ catalyst.

AgBr/B-P-CN Nanosheets

Next, the final AgBr/B-P-CN nanosheets were synthesized. 2g of B-P-CN powder was dissolved in a mixture of 5ml distilled water and 20 ml ethanol and kept under vigorous stirring for 2h. Next, a certain mass percent of AgBr nanoparticles were added and the mixture was kept under vigorous stirring for 2h. The mixture was then dried in an oven at 80° C and calcined at 500° C for 2h yielding AgBr/B-P-CN nanocomposite.

Catalyst Testing

Finally, the catalysts were tested for 4 hours under sunlight conditions. This time period was chosen to demonstrate the long term performance of the catalysts but also fit within time constraints.(Zhuxing, S. et. al., 2018) This included leaving the catalysts in water in a stainless steel, air-tight container with a clear plastic top, CO₂ bubbling capabilities and a port for gas extraction. The joints were sealed with inert silicon. A glass container would be preferable to prevent any unwanted side reactions or gas contamination however, borosilicate glass (used in most lab glassware) would block a large portion of the spectrum that the catalysts would absorb. To remedy this, a special type of glass would be required but this was not possible due to monetary constraints. In the beginning, CO₂ will be bubbled in to purge the reactor of any air and to achieve atmospheric pressure. For the first 1 hour the gas was sampled every 15 minutes and analysed through gas chromatography. Then gas will be sampled every 30 minutes and analysed in the same way.

Gas chromatography that is used in this experiment works by passing the gasses through a small capillary tube lined with a substance designed to slow the gasses down. Different gasses are affected to a different extent based on factors such as molecule size and polarity (relative

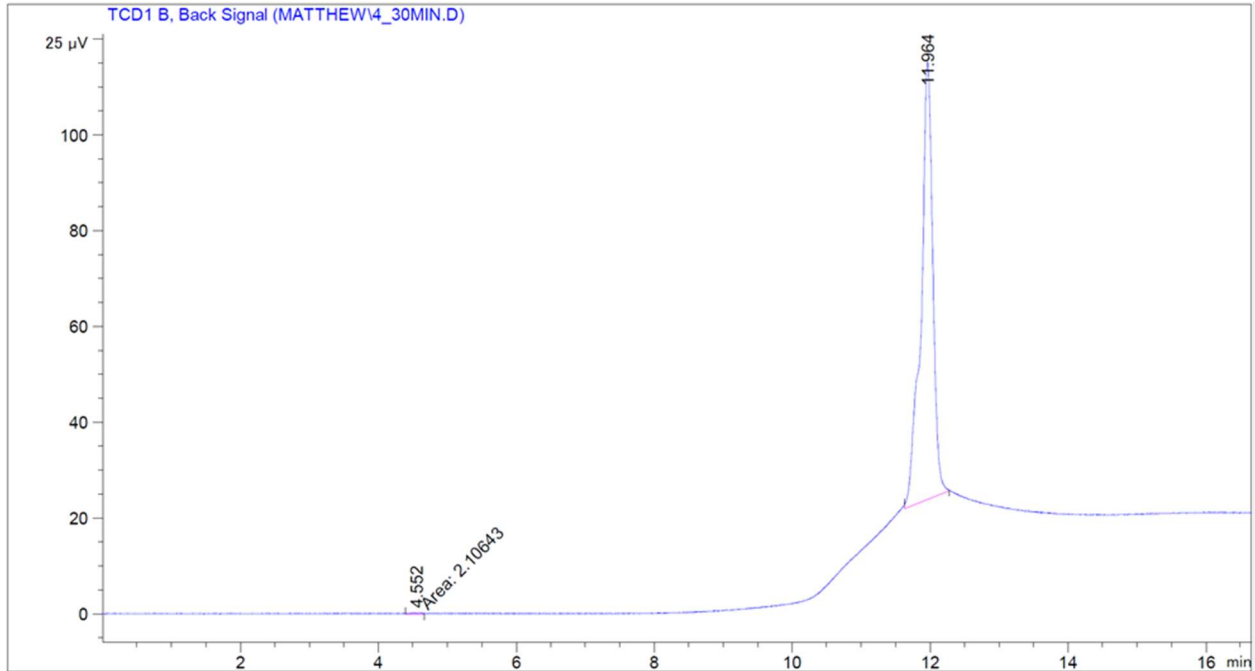
charge across a molecule). Since the gasses are traveling at different speeds through the tube, they separate and arrive at the gas detector at different times. The gas chromatograph then generates a graph that shows how much gas was detected at different points in time. A particular gas will always appear at the same time on the graph, provided the gas chromatograph setup remains consistent. This means that by running a known sample through the gas chromatograph, the time at which a gas appears can be recorded and this gas will be identified in future trials. This is how gasses will be identified in this experiment.

Through gas chromatography, the percent composition of products of CO₂ reduction will be measured. The rate at which these products are produced for each catalyst will be compared to determine the most effective catalyst. After each sampling, CO₂ will be bubbled in to hold the pressure at 1 atm.

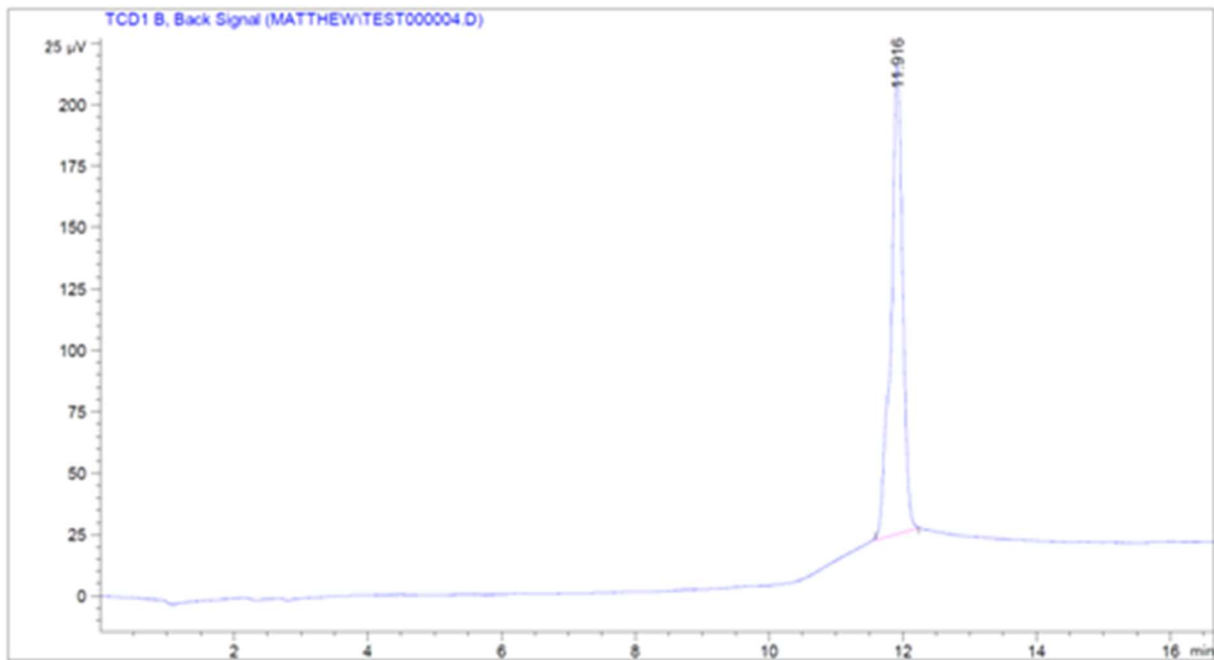
All reagents purchased were of reagent grade.

Through every step proper safety equipment was used including, but not limited to, safety glasses, gloves, and a lab coat.

Through every step, beakers, pipettes and other various glassware were used.

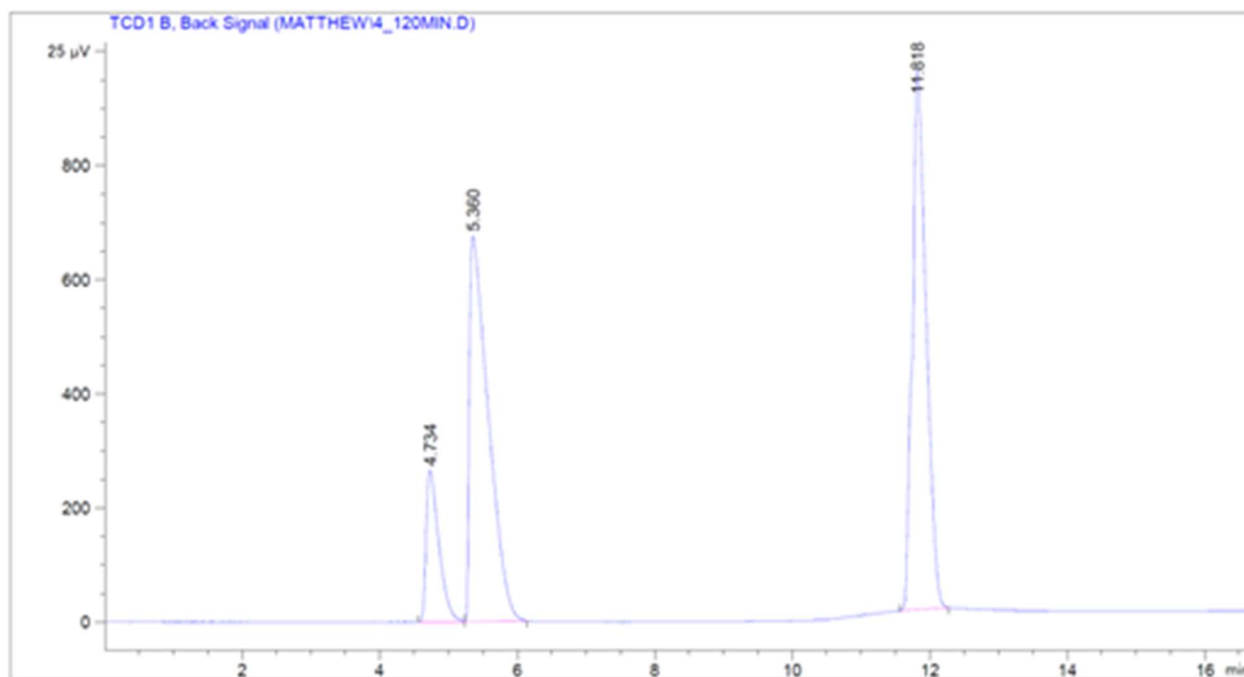


Graph 1– (Courtesy student) This graph shows the consistent large peak at just under 12 minutes that represents CO₂ but it also shows a much smaller yet significant peak at 4.6 minutes. This appears on multiple graphs but is believed to be contamination from a freshly changed septum since it is not present in samples tested before this sample.

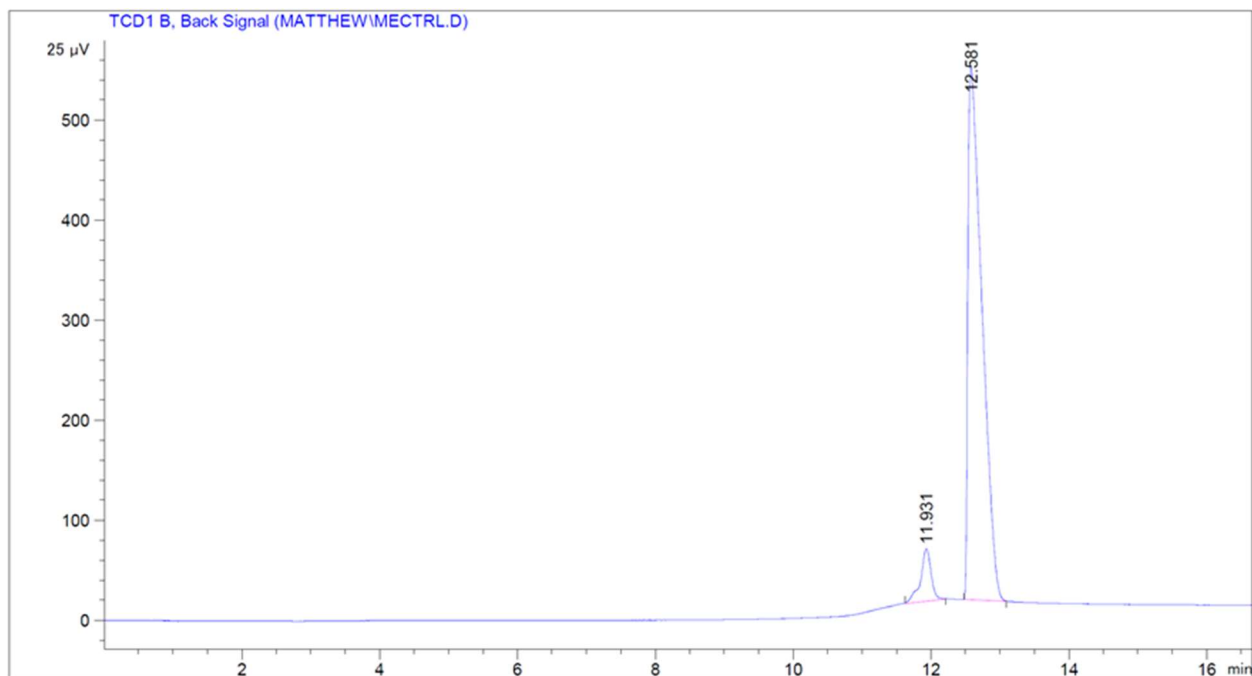


Graph 2– (Courtesy student) This graph shows a trial with pure CO₂ that was run to ensure that the spike at 11.9

minutes on all the trials was, in fact, CO₂



Graph 3– (Courtesy student) During this run on the gas chromatograph, the septum broke and allowed contaminants to enter the inlet. A septum is a small rubber disk that is clamped onto the inlet of the gas chromatograph via a special nut to seal the inlet. The needle of the syringe used for sampling is inserted through the septum and into the inlet and sequentially injected. When the needle is removed, the rubber closes around where the needle used to be and maintains the seal. Over time, or with improper use, the septum can fail and allow contaminants in. That is what is depicted here.



Graph 4— (Courtesy student) This is a trial of natural gas composed mostly of methane. A spike at 12.6 minutes can now be identified as methane.



Figure 2– (*Courtesy student*) This picture is of the substance after DCDA is calcined for the first time. It is mostly comprised of graphitic carbon nitride but still contains a significant amount of DCDA. The porous structure is a result of gaseous ammonia escaping and leaving pores during the reaction.

Results

All synthesized catalysts produced color and appearance results consistent with past literature. The nanoparticles had the ability to pass through a 100 nm membrane filter, indicating an upper limit on their size. Consistent peaks for CO₂ were found at 11.9 min, this was indicated by a control test with pure CO₂ shown on graph 2. No methane production was shown in gas chromatography. Graph 4 shows the results when natural gas (95% methane) was tested. The biggest peak is methane and indicates where a methane peak would be on the results of other

samples(12.6 min). Graph 1 represents a typical sample and shows no peak at 12.6 minutes. An unknown gas is shown in several graphs at 4.6 min. Graph 1 shows one such sample but it is shown on other graphs not included for readability. This is unidentifiable without a mass spectrometer or a reference. This could be potential contamination but it is unlikely because it occurred on multiple samples. A failed septum led to contamination on 3 trials. Graph 3 is an example of this.

Discussion

This experiment has been inconclusive as of yet. There was no evidence of methane production even from controls that have been shown to successfully reduce CO₂ into methane in past experiments. This can be seen in Graph 1, a typical trial. There are several possible sources of this discrepancy. Firstly, the sensitivity of the gas chromatograph should be addressed. The gas chromatograph was able to sense gasses consistently down to .01% in concentration. This would be sufficient as methane was found in concentrations of at least .2% in past literature. This indicates that the sensitivity of the gas chromatograph was likely not the problem.

Another potential reason for the lack of methane is the source of catalyst stimulus. In the literature referenced, the two most common light sources were a xenon arc lamp and the sun. The sun was chosen due the lack of availability of an arc lamp. Unfortunately, this option is less consistent and did not get consistent sun for the full four hours, occasionally the sun would be hindered by a cloud. Finally, the arc lamp is simply more intense than the sun which would have theoretically yielded more methane.

A final consideration on the results is the reaction vessel itself. While the reaction vessel was custom made and did have a lot of consideration put into it, monetary constraints limited the

reaction vessel. Firstly, the clear topper of the reaction vessel was made of plastic wrap and sealed with a rubber band. Ideally this would have been made of quartz glass or UV transmitting acrylic and glued permanently on. This would not only increase the amount of light that came in, but also ensure a seal that would prevent contamination. For it to be permanently glued on, there would have to be another way to bubble in CO₂ which would add further complication. Had these considerations been possible for the reaction vessel and light source, there may have been more promising results from the experiment as a whole. This is something that is currently being pursued in this project and that will continue to be pursued.

It is also important to note that there is an unidentified gas in small amounts at 4.6 minutes. This is visible in graph 1. Not all trials are shown for readability but the peak is present in several other graphs. It is possible that this is a product of CO₂ reduction but further testing would be required. Gas chromatographs on their own can only compare samples. Thus, without a matching control sample, the gas chromatograph cannot positively identify this substance. It is possible for a mass spectrometer to be attached to a gas chromatograph in order to be able to identify any substance passed through the gas chromatograph. This setup is very expensive and not viable in this experiment but could be a valuable next step.

Classification was also a challenge for this experiment. The standard method of classification for graphitic carbon nitride is x-ray diffraction spectroscopy. This was not available for this project. The graphitic carbon nitride was classified using physical and chemical characteristics such as color and solubility and reaction byproducts (Figure 2). The synthesis of the graphitic carbon nitride was consistent with past literature and the expected ammonia gas evolution was observed during calcification. Classification of the AgBr nanoparticles was more conclusive. The nanoparticles passed through a 100nm membrane filter indicating a maximum

size. With the addition of nitric acid and then hydrochloric acid, the precipitation of AgCl was observed, indicating the presence of silver in the particles.

Some errors and interesting results were observed through gas chromatography. Firstly, the septum, which seals the gas chromatograph inlet but also allows a needle to be inserted, broke 3 times. This is likely due to the needles used being too large. This led to contamination and extraneous peaks as seen in graph 3. There was also a small but significant peak that occurred at 4.6 minutes in several trials. All of these trials occurred after the septum was replaced and since the peak occurred only in the 30 minute samples, it was likely contamination from volatiles that were evaporated off the new septum.

Future Directions

While this research has yet to identify whether AgBr nanoparticles improve CO₂ reduction for boron and phosphorus doped graphitic carbon nitride, it does present a good base for future directions. It is important to note that although many improvements are identified, the experiment conducted was still consistent with scientific standards and supporting literature. The future directions are mostly limited to two areas: classification and data collection.

Classification techniques are the first area to be improved in the future. It stands that the most simple explanation for the lack of observed methane evolution is that g-C₃N₄ was not, in fact, the product used for the rest of the synthesis. While there were several properties indicating g-C₃N₄ as the product, such as color and reaction byproducts, as well as no factors indicating otherwise, it is impossible to say with great certainty that the product was g-C₃N₄ without x-ray diffraction data. All other synthesized substances are similarly uncertain, while all evidence

suggests that the products are what they are meant to be, the spectrometry or x-ray diffraction data is not there to positively characterize the products. In the future, x-ray diffraction and ultraviolet/visible spectrometry would be the first next step in order to rule out the possibility of the catalyst not existing in the reaction chamber.

In terms of data collection, several changes will be made in the future, each providing a small improvement from the current set up. First, a xenon arc lamp will be employed for several reasons. Using a constant source of light will not only allow for much higher controllability of the experiment, but also allow the intensity of the light source to be known. By knowing the intensity of the light source, the efficiency of the catalyst can be more precisely calculated. Additionally, the use of a xenon arc lamp will allow for the experiment to take place inside while closely modeling the wavelengths of light emitted by the sun. This is advantageous for the next future improvement.

Manual injection of sample into the gas chromatograph allows for errors such as contamination and wide or false peaks. By switching to automatic sampling, the time between injections and the amount of the injection can be precisely controlled. Additionally, automatic sampling creates sharper peaks and allows the experiment to be conducted for larger amounts of time (the experimenter will not have to be present during experimentation).

Another improvement to the gas chromatograph setup would be to add a mass spectrometer. In this case, after gasses pass through the gas chromatograph they would enter the mass spectrometer and be identified. This would make identification easier and not reliant on controls. Additionally, unidentified peaks such as the one at 4.6 minutes on graph 1 would be

able to be identified. This could show a different product of CO₂ reduction than the expected methane.

Several more changes will be made to the reaction chamber. As previously detailed, utilising UV-transmitting acrylic could have an impact on the performance of the catalyst by allowing more ultraviolet light to interact with the catalyst. For this to be permanently affixed and if longer trials were desired, a hose would be required at the bottom of each chamber to automatically bubble in CO₂. It is important for it to be bubbled in so that some can be dissolved to interact with the catalyst. A hose would also have to be added to the side of each chamber for automatic sampling.

All of these improvements will help the experiment be more successful in the future but are not required for a successful experiment. Perhaps adding only some of these improvements will help yield more useful results but it is impossible to know until they are put into practice.

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