

The Effect of AgBr Nanoparticles on Boron and Phosphorous Doped Graphitic Carbon Nitride CO2 Reduction Efficiency for Artificial Photosynthesis

Introduction

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Artificial photosynthesis is a process that utilizes 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. 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. 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.

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. According to Raziqie et al. P-B co-doping and SnO₂ coupling improve g-C₃N₄ catalysis by a factor of approximately 8. 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. 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. 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.

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. 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.

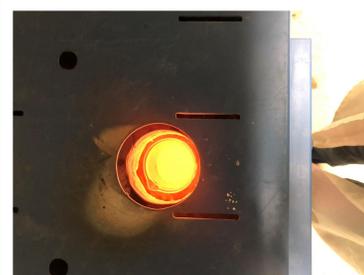


Figure 1 – (Courtesy student) This depicts the DCDA as it is being calcined into graphitic carbon nitride.

Figure 2 – (Courtesy student) This picture is of the substance after it 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.

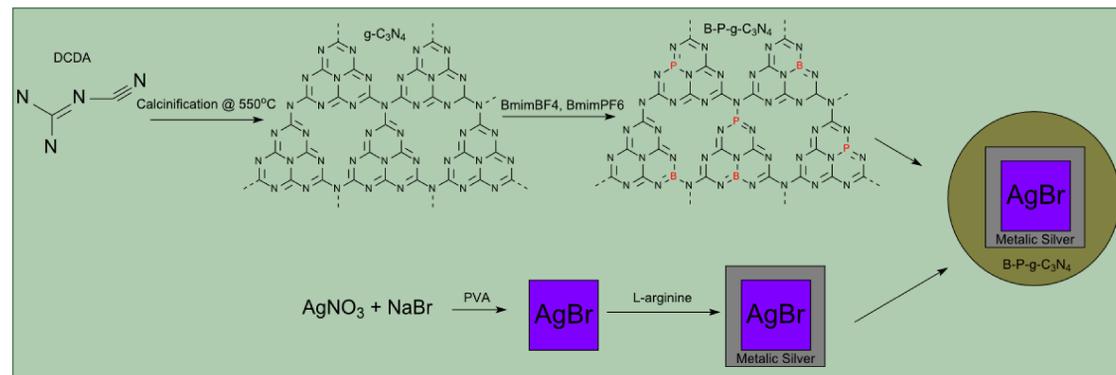


Figure 3 – (Courtesy student) This reaction scheme demonstrates the entire synthesis accomplished by this project. It shows the process of synthesizing both the g-C₃N₄ and the AgBr nanoparticles and combining them.

Hypothesis

If silver bromide nanoparticles are added in mass percents of 4%, 6%, and 8%, to a boron and phosphorous doped graphitic carbon nitride catalyst, The 8% AgBr catalyst will perform the best but only marginally better than the 6% AgBr because the AgBr will work with the g-C₃N₄ to add surface area and increase absorbance but after 6%, the extent of these effects is minimized.

Methods

CN Nanosheets

50g of DCDA was heated in a ceramic crucible in a muffle furnace at 550° C for 4h. The material was then be cooled to room temperature, ground into a powder, 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.(Raziqie F., et al., 2017)

B-P-CN Nanosheets

Next, the nanosheets were co-doped with Boron and Phosphorus, achieved using ionic liquids. This is the only method of doping CN nanosheets that has been successful in the past. A certain amount of 1-butyl-3-methyl imidazolium-tetra-fluoroborate (BmimBF₄) and 1-butyl-3-methyl imidazoliumhexafluorophosphate (BmimPF₆) were dissolved into 50 ml of deionized water and stirred for 1h. Subsequently, 4g of DCDA were added to the mixture and it will be heated to 100° C until all water had completely evaporated. The resulting white solid was be 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 recalined at 550° C for 3h to obtain B-P-CN nanosheets.

AgBr Nanoparticles

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) 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. The reaction proceeded for 30 minutes. Then, L-Arginine was be added as a reducing agent and the reaction continued for an additional 45 minutes.

AgBr/B-P-CN Nanosheets

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

The reaction vessel was a stainless steel pipe with a diameter of 2 inches. This was attached to a stainless steel base plate via silicone adhesive. Several pipes were attached to the same base plate to allow for simultaneous testing. Each pipe had a hole drilled in the side to allow for the use of a stopper. A syringe needle then could be inserted into the vessel to extract gas without breaking the seal. On the top of each pipe was a piece of plastic wrap sealed with a rubber band. Plastic wrap was chose for its superior UV transmitting capabilities. The alternatives to plastic wrap were quartz glass and UV transmitting acrylic which were both prohibitively expensive. 1g of each catalyst was added to 15ml of deionized water in a reaction vessel. CO₂ was bubbled in and the reaction chambers were sealed with plastic wrap. The reaction chambers were placed in the sun from 1:30pm to 5:30pm. For the first hour, a .5ml sample of the gas was taken every 15 minute. For the rest of the test, a sample was taken ever 30 minutes. These samples were then analyzed in a gas chromatograph with helium as a eluent. The samples were anlyzed with a low flow rate through a capillary column at temperatures from 35 C to 150 C.

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.
 - A control test with pure CO₂ is shown on graph 2.
- No methane production was shown in gas chromatography.
 - Graph 1 represents a typical sample.
 - 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).
- An unknown gas is shown in several graphs at 4.6 min.
 - Graph 1 shows one such sample.
 - This is unidentifiable without a mass spectrometer or a reference..
 - Potential contamination but it occurred on multiple samples.
- A failed septum lead to contamination on several graphs.
 - 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. 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 he to be another way to bubble in CO₂ which would add further complication. Had these consideration 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.

Classification was also a challenge for this experiment. The standard method of classification for graphitic carbon nitride is x-ray defraction spectroscopy. This was not available for this project. The graphitic carbon nitride was classified using physical and chemical characteristics such as color and solubility. 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 see 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 hadn't evaporated off the new septum.

References

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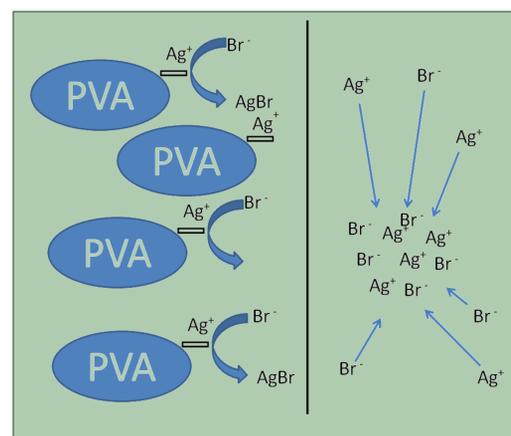
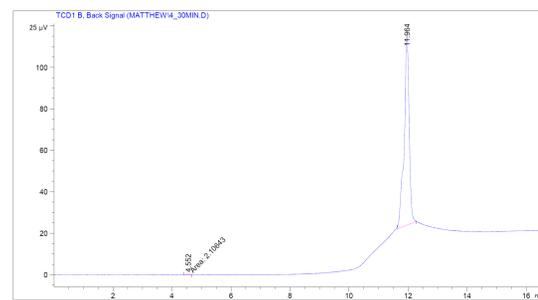
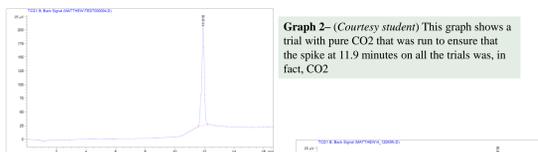


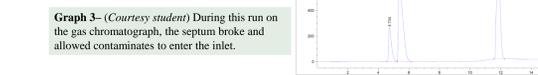
Figure 4 – (Courtesy student) This diagram indicates the importance of including PVA for synthesizing the nanoparticles. While simply mixing AgNO₃ and NaBr would result in AgBr, they would be much too big for this project. The addition of the PVA holds the Ag ions until a Br ion comes close enough to pick it up. This slower process results in much smaller particles because the Ag ions cant rush into a glob, they must be picked up by a Br ion.



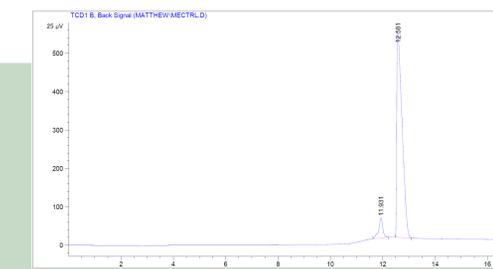
Graph 1 – (Courtesy student) This graph shows the consistent large peak at just under 12 minutes that represents CO₂ but it also shows a much smaller yet significant peak at 4.6 minutes. This appears on multiple graphs but is believed to be contamination from a freshly changed septum since it is not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



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.