Introduction and Background

Photocatalysis - the use of light to drive chemical reactions - is a viable route toward forming sustainable chemical fuel sources. In traditional photocatalysis, an absorber material promotes oxidation and reduction processes of interest. One way to enhance photocatalysis is to separate the different photocatalytic steps. This can be done using a bipolar membrane (BPM) - a polymer membrane with cation-selective and anion selective layers. This affords fine tuned control over the parameters that influence reduction and oxidation (e.g. pH, concentration, etc.) for optimizing the overall process. To date, it has been shown that light-absorbing semiconductors such as CdS and electron-acceptors such as gold particles can be loaded into BPMs and used for photocatalysis. However, this provides only a limited set of photo-active materials for BPM-based photocatalysis. Finding new semiconductor light absorbs that are compatible with the BPM is thus of interest. The theory behind this exploratory research can be summarized below in Figure 1.

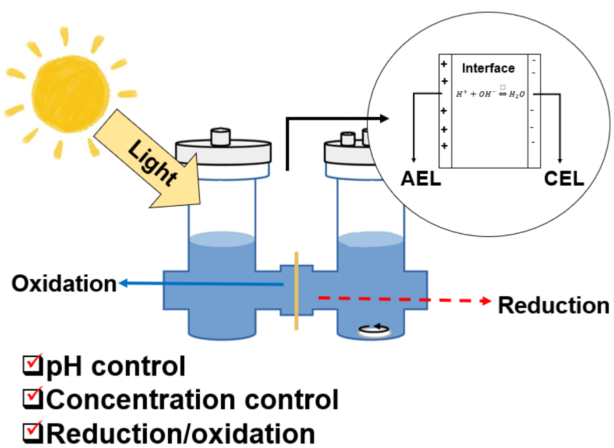


Figure 1. General schematic of Bipolar Membrane functionality

In this work, we investigated methods to load two ternary semiconductors - $AgInS_2$ and $CsPbBr_3$ - into BPM films. $AgInS_2$ provides a non-toxic alternative to traditional semiconductors, and $CsPbBr_3$, while it contains lead (Pb), has several beneficial properties for photocatalysis. The general method for formation of ternary semiconductors in the BPM was to first soak the films in a solution to load the cations (e.g. Ag^+ or Cs^+), then react that film to form an intermediate compound (Ag_2S or CsBr). Next, cation exchange reactions were employed to form the final material - either reaction with indium to form $AgInS_2$ or reaction with lead to form $CsPbBr_3$. The general methodology is summarized by Figure 2 and 3, respectively for each of the semiconductors. Although successful formation of Ag_2S was confirmed via UV-visible spectroscopy, the conversion to $AgInS_2$ so far has remained elusive. Similarly, formation of CsBr within the BPM was successful (confirmed via UV-vis), but the cation exchange to $CsPbBr_3$ has proved difficult.

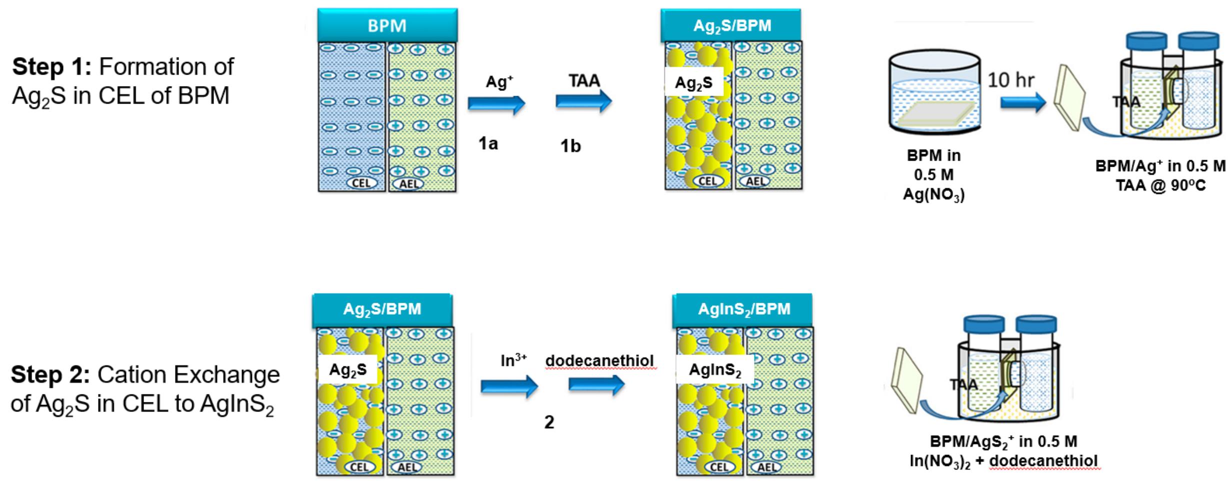


Figure 2. Synthesis Procedure for $AgInS_2$ in BPM

Synthesis Procedures for $CsPbBr_3$ in Bipolar Membrane (BPM)

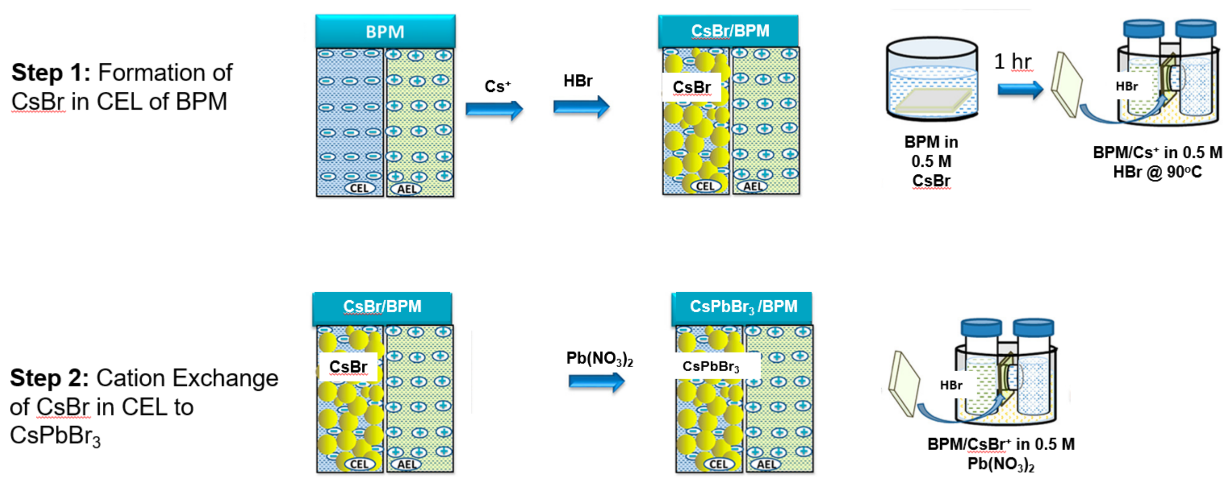


Figure 3. Synthesis Procedure of $CsPbBr_3$ in BPM

Future directions will focus on adding chemical catalysts to promote cation exchange. Once successful, photocatalytic reduction of a model dye compound such as methyl viologen will be done to demonstrate the viability of loading ternary semiconductors within the BPM.

Data and Results

When first experimenting with bipolar membranes in silver nitrate, one of the first points noted was the effect of light on the loading process of silver onto the membrane. Since silver nitrate is light-sensitive, the mixture had to be contained in the dark, avoiding ambient light conditions at all costs.

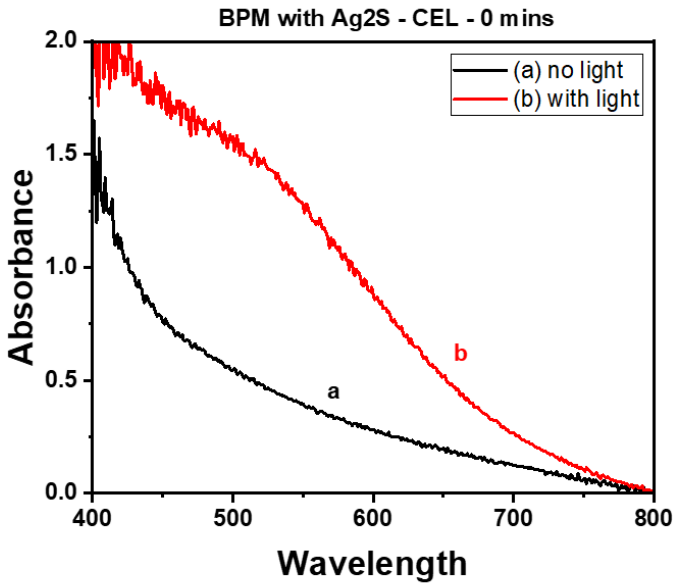
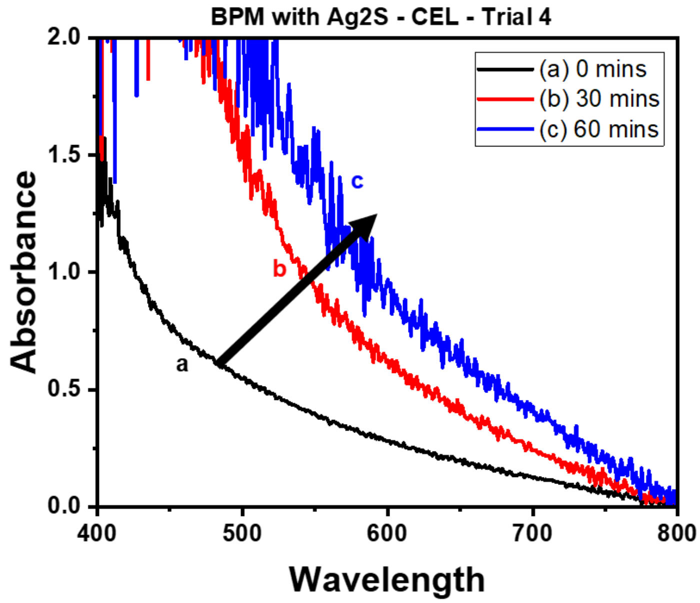


Figure 4. Effect of light on BPM with silver nitrate

As shown above, there is less scattering and a much better fitted curve of absorbance when exposed to no light, as to the one in ambient light conditions.The solution exposed to light has more absorption because there are likely silver ions formed due to photoreduction.

The next step of the procedure was to then use the BPM with silver ions and react with TAA for a certain amount of time. Since there is not really a given range known to work efficiently with TAA and the silver ions, more trial and error had to be done. Based on the data collected, the best fit curve was the 30 minute reaction time with TAA. Longer than 30 minutes caused degradation of the film and the absorbance was too high to measure. The data is shown below in Figure 5.



BPM was soaked in a silver nitrate solution overnight in an environment with no light.
Then, the BPM underwent reaction with TAA for 30 min intervals for up to 60 mins.

Figure 5. BPM in silver nitrate after reacting with TAA

Since the silver ions successfully reacted with TAA, the sudden increase in the graph from 0 mins to 30 mins suggests the formation of Ag_2S, which will be confirmed with XRD eventually. Based on the assumption that there is Ag_2S successfully loaded onto the BPM, the next and final step is to react the same film with indium nitrate and dodecanethiol in a toluene and methanol solution. The indium exchange is measured for different time periods to observe how long it ideally takes for the indium to fully exchange with the silver sulfide on the BPM. The data is best summarized in Figure 6 below.

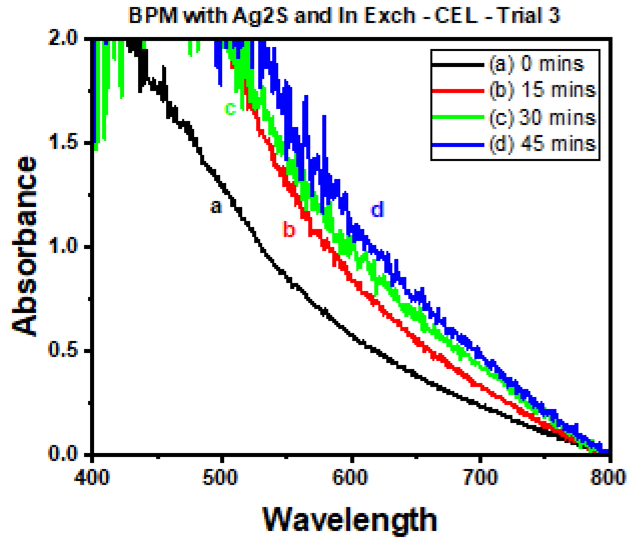


Figure 6. BPM with Ag_2S and indium exchange for 0 to 45 minutes

The shift is not entirely significant and XRD is needed in order to confirm the results. In the meantime, an adaptive synthesis was used to form the same result, but hopefully for more distinctive results. In the adaptive synthesis, silver nitrate and indium nitrate are co-loaded, instead of the multi-step process, there is one step involved. As expected, the results are much more distinctive and clear.

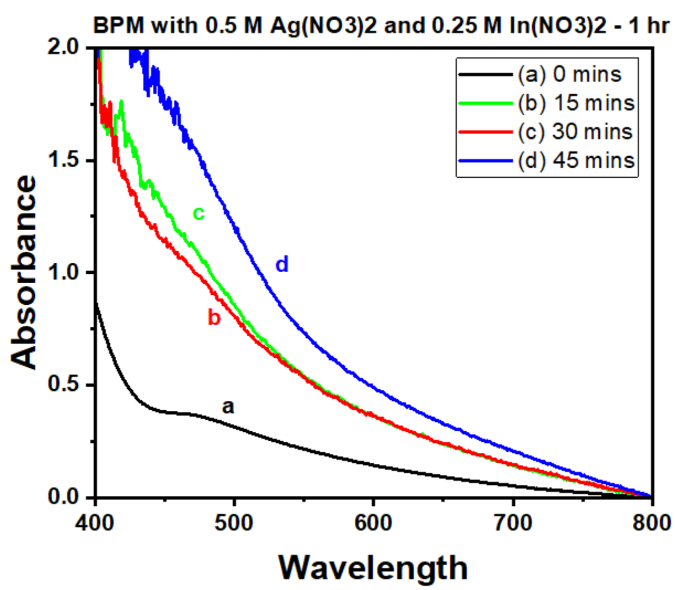


Figure 7. Co-loading synthesis of silver nitrate and indium nitrate

Different concentrations were used and the results were quite similar to each other. The different concentrations only changed the absorption by a small amount for each.

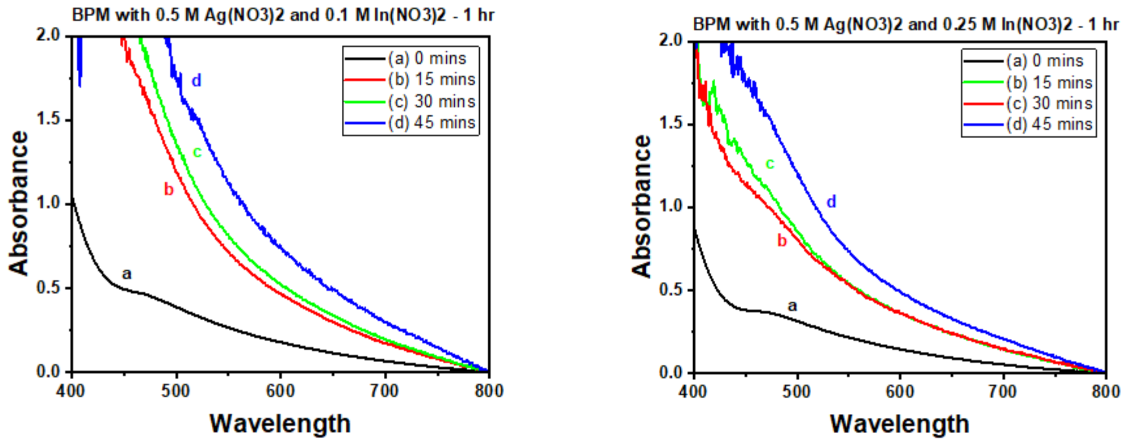


Figure 8 and 9. Different concentrations of co-loading silver nitrate and indium nitrate

These results were promising, and so a different ternary semiconductor was tested. As mentioned before, a similar procedure was used with different materials and the results are shown below in Figure 10.

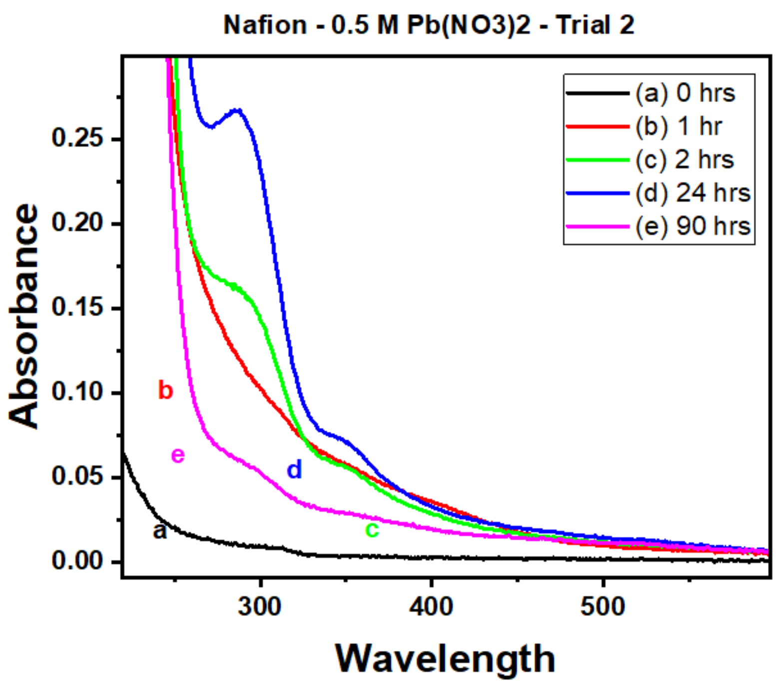


Figure 10. Nafion soaked in CsBr and HBr, then reacted with $Pb(NO_3)_2$

Given a proper amount of time, there is a peak rising near 300 nm. The peak resembles a similar peak of Cs_4PbBr_6, which is based on literature shown below.

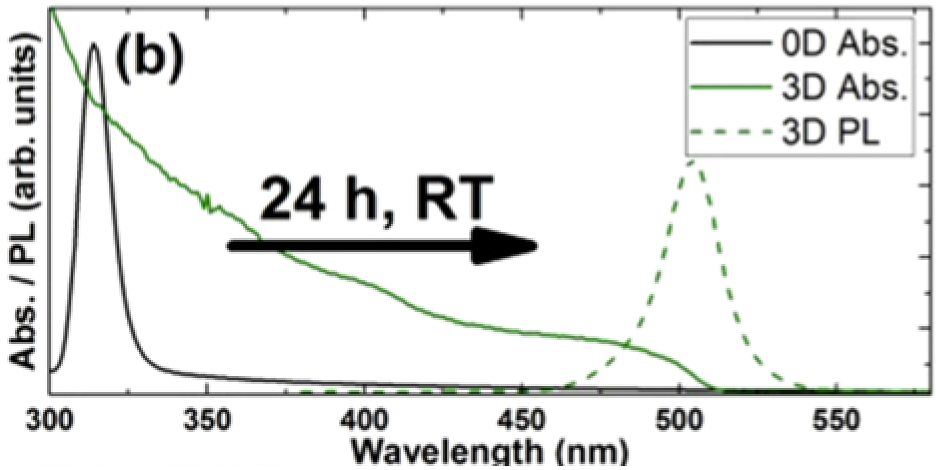


Figure 11. Literature resemblance of peak

This polymorph can easily be converted to the ternary semiconductor that we desire, which is $CsPbBr_3$ by heating the polymorph to 150 C for a certain amount of time. More testing is needed in order to prove this but the results are promising.

In conclusion, silver and cesium ions were successfully loaded onto the BPM films for the formation of ternary semiconductors. Silver indium sulfide was lightly formed when using a mixture of 0.5 silver nitrate and 0.5 M indium nitrate, and reacting with the BPM simultaneously in a co-loading process. Loading Cs_4PbBr_6 was successful and will be converted to $CsPbBr_3$. Other semiconductors will be tested, including $CuInS_2$.