METHYLENE BLUE DEGRADATION
WITH SODIUM BISMUTH OXIDE
NANOPARTICLES

by

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Abstract

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The effectiveness of Sodium Bismuth Oxide nanoparticles as a photocatalyst was tested by applying it to the degradation of methylene blue. The nanoparticles had increased effectiveness with increased concentration and reaction time. However, when the particles were microwaved, there was not a significant change in the effectiveness of the nanoparticles. Therefore, these nanoparticles are not a good candidate for microwave induced photodynamic therapy, but they could be used on their own for other applications.

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Chapter 1

INTRODUCTION

Microwave Induced Photodynamic Therapy (MIPDT) is a new form of cancer treatment being developed by our group. This is very important because cancer is one of the leading causes of death around the world. Also, current cancer treatments prevent patients from being able to do everyday activities and are very painful and miserable. Photodynamic therapy is a method already used to treat skin cancers. Photodynamic therapy involves putting a photosensitive chemical, typically PPIX, on the cancerous area of the skin, then shining visible light on the treated area in order to kill the cancer cells. This is a very effective treatment of skin cancer, but it cannot be applied to deep cancers because visible light cannot penetrate into the body. The idea behind MIPDT is that nanoparticles are delivered to a cancerous tumor and are then activated to produce singlet oxygen, killing the cancer cells. This significantly decreases the side effects of currently used cancer treatments such as chemotherapy and radiation therapy, because it specifically targets cancer cells instead of attacking all cells [4].

In these experiments, methylene blue was used as a dye to determine the photocatalytic capabilities of sodium bismuth oxide ($NaBiO_3$) nanoparticles. Previous experiments have been done with titanium dioxide particles and gold nanoparticles. When nanoparticles are added to the methylene blue, they made the solution clear. The effectiveness of the nanoparticles as photocatalysts is measured by comparing the absorbance spectra of methylene blue alone and that of the solution containing both methylene blue and nanoparticles. The absorbance spectra are measured using an UV-Visible spectrophotometer. A spectrophotometer is an instrument that measures the amount of photons that pass through a sample solution. It then creates an absorbance spectrum based on the following formula, where I is intensity.

$$Absorbance = -\log(\frac{I_{transmitted}}{I_{initial}})$$

Absorbance is a unitless quantity that is often used to determine the concentration of a known chemical in a solution using the Beer-Lambert Law. A low absorbance compared to that of regular methylene blue means that there is a lower concentration of the dye which implies that the nanoparticles were effective photocatalysts. The effect of microwaves on the nanoparticles was also measured. The concentration of nanoparticles, reaction time, and time microwaved were all varied in order to study their effects on the degradation of methylene blue. A list of possible chemical equations describing the degradation is given in reference [2].

In reference [2], titanium dioxide nanoparticles were used in the photocatalytic degradation of methylene blue. This paper was used to determine the general method of mixing solutions of methylene blue and nanoparticles. More specifically the ratio of methylene blue powder to water ratio was determined by following the 72 M solution in this paper. This paper also provided a general idea of how much of a solution of nanoparticles is needed to degrade methylene blue. The TiO2 nanoparticles were successful in removing the color from the methylene blue.

In reference [1], TiO2 nanoparticles were still used for degradation of methylene blue, however this reference focused more on the effect of UV irradiation on the solution. A similar procedure was followed in order to study the effects of microwaves on the solution. It also gave me an example of what a methylene blue absorption spectrum should look like. I used this to make sure the results I was getting were accurate.

Chapter 2

METHODS AND MATERIALS

I used Methylene blue solution with 72 M concentration. I also used sodium bismuth oxide nanoparticles synthesized by Dr. Lun Ma. The NaBiO3 nanoparticles are synthesized by the wet chemistry method. Briefly, 20 ml sodium hypochlorite solution is mixed with 20 ml DI water and loaded into a 100 ml flask, followed by the addition of 1.6g sodium hydroxide under vigorous stirring. Then, 2.4 mg poly(ethylene glycol) methyl ether thiol are added into the solution before 1.2 ml 0.1M bismuth nitrate is dropped into reaction. The reaction solution is then kept under stirring for 3 hours. Finally, the obtained nanoparticles are washed using DI water 3 times by centrifuging.

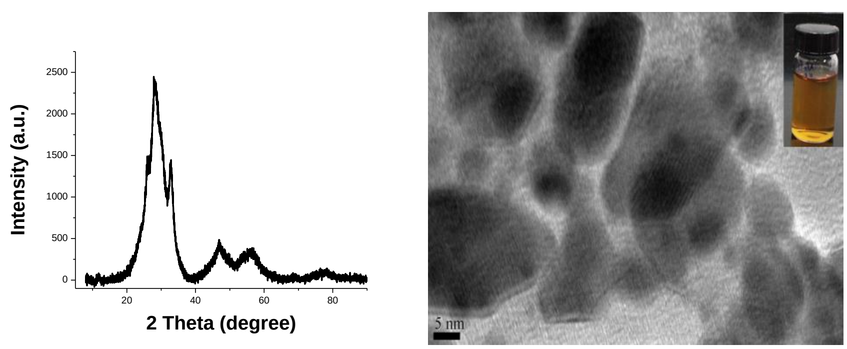

Figure 2-1. XRD pattern (left) and TEM image (right) of the NaBiO3 nanoparticles. The inset is a photo picture of the NaBiO3 nanoparticle aqueous solution.

The XRD pattern of our nanoparticles presented in Figure 2-1(left) reveals a cubic structure of NaBiO3 (JCPDS, no. 81-2500) with space group Fd-3m. The main diffraction lines are indexed with the planes of (222), (400), (311), (440), and (622). As a result of the size effect, the XRD peaks are broadened. Based on the Debye–Scherrer formula, the average crystal size is estimated at about 24 nm. The TEM images of $NaBiO_3$ nanoparticles are shown in Figure 2-1 (right). The mean size of these nanoparticles is about 25 nm, which is consistent with the result estimated by XRD. The majority of the obtained nanoparticles are in spherical-like shapes. The water solubility is very good as seen in the inset in Figure 2-1 (right).

Every sample I made contained .8 ml of methylene blue solution and varied amounts of deionized water and the $NaBiO_3$ solution. The highest amount of nanoparticle solution was .4 ml. When less $NaBiO_3$ was used the volume was replaced with DI water to make the total volume the same for each sample. Each sample was then diluted with another 2 ml of water for the purpose of measuring the absorption spectra. A Shimadzu UV-Vis spectrophotometer was used to measure the absorption spectra of all of the samples.

The first part of the experiments was varying the concentration of nanoparticles. Five samples were made. Each of the five samples contained .8 ml of methylene blue solution. The control also contained 2.4 ml of DI water. The next sample had .1 ml of $NaBiO_3$ solution and 2.3 ml of DI water. The third sample had .2 ml of $NaBiO_3$ solution and 2.2 ml of water. The fourth sample had .3 ml of $NaBiO_3$ solution and 2.1 ml of water. The last sample had .4 ml of $NaBiO_3$ and 2.0 ml of water. After mixing, the samples were left in the lab under room light for about 24 hours to give the solution plenty of time to fully react. The samples were then measured with the spectrophotometer. This process was repeated 5 times in order to find an average and standard deviation.

For the next part, only one sample was made. It was comprised of .8 ml methylene blue, .4 ml $NaBiO_3$, and 2.0 ml water. This sample was then measured immediately after mixing and once every hour for five hours. This was also repeated five times to find an average absorption peak.

The last part measured the effect of microwaves on the samples. Three different concentrations were used. The first was .8 ml methylene blue and 2.4 ml of water. The second was .8 ml methylene blue, .2 ml $NaBiO_3$, and 2.2 ml water. The third was .8 ml methylene blue, .4 $NaBiO_3$, and 2.0 ml water. Six samples of each concentration were made. Immediately after mixing, the samples were microwaved for 0-5 minutes in one minute increments at 20 W. After microwaving, the samples were given 24 hours to fully react, and then they were measured. All of these were also repeated five times each.

Each absorbance was divided by the absorbance of a control sample made and measured at the same time. This is because the results of the absorbance varied based on the amount of ambient light in the room. The nanoparticles as photocatalysts are activated by room light. If the samples were exposed to more light before their measurement, the solution was less blue and therefore had a lower absorbance. In order to compensate for the changes in room lighting, the absorbance of each sample was compared to the absorbance of the control sample that was exposed to the same lighting. An improvement to this experiment would be to have controlled, consistent lighting on the samples. However, a dark box will not work since the nanoparticles are activated by visible light.

Chapter 3

RESULTS

Figure 3-1 shows the absorbance spectrum of methylene blue. All spectra found in this experiment have peaks in the same places. The only differences between the spectra are the height (intensity) of the peaks. Therefore, future figures will show the maximum absorption only so the trend is clear. As the sample becomes less blue and clearer, the intensity of the absorption decreases. Therefore points with lower absorbance correspond to samples that have more degradation.

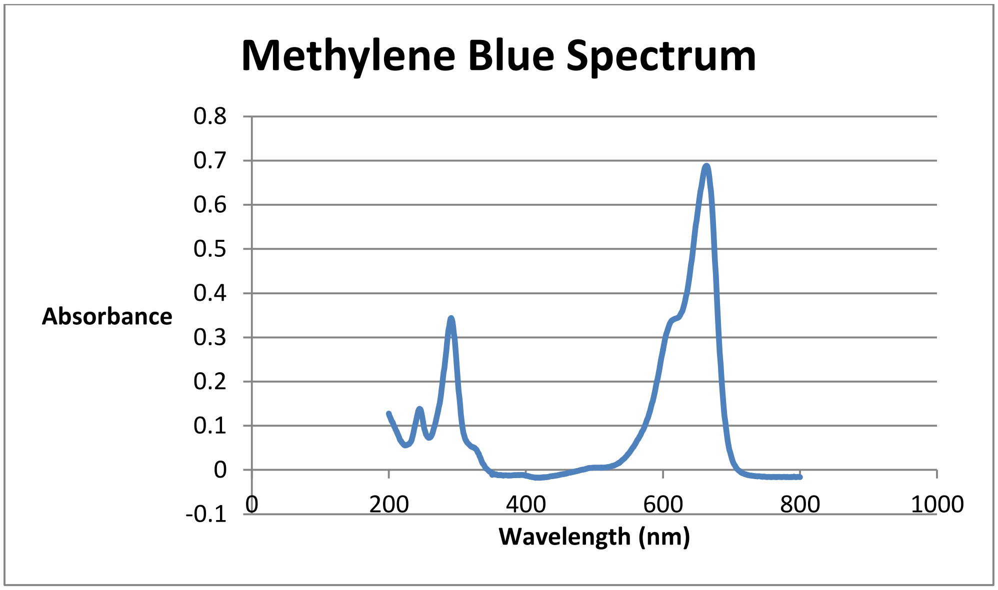

Figure 3-1: Absorption Spectrum of Methylene Blue

Varied Concentration

When the concentration of nanoparticles increased, the absorption, for the most part, decreased. Figure 3-2 shows the change in the peak absorption as concentration increased. When small amounts of nanoparticles were added to the methylene blue, very little change to the absorption occurred. As more nanoparticles were added, the decrease in absorption becomes more significant. To the naked eye, the samples with 0.4 ml of nanoparticles appeared to be completely clear, and resembled water. There was an obvious visible gradient between the samples.

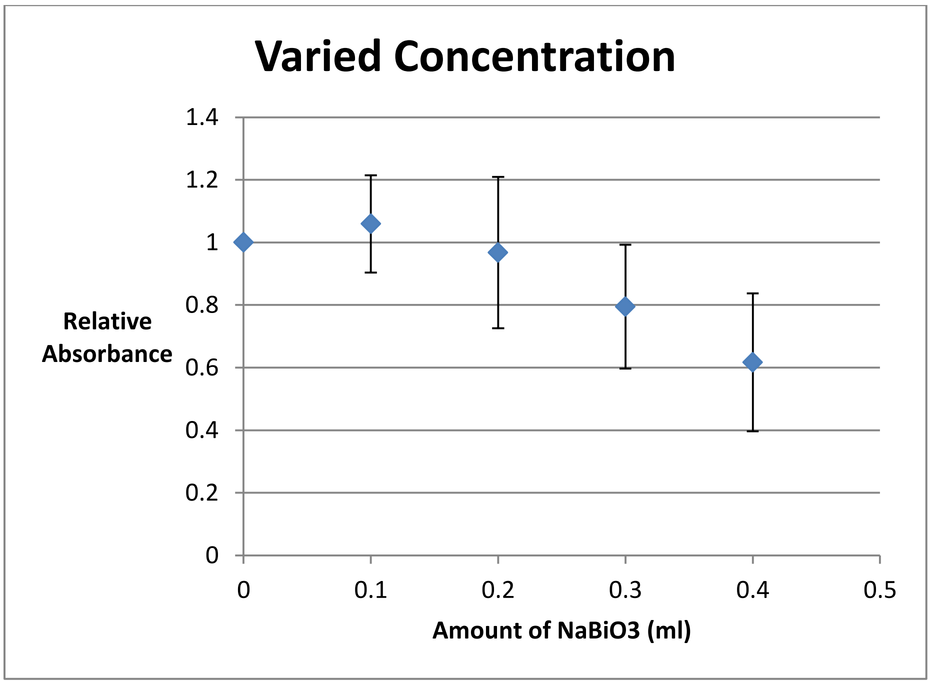

Figure 3-2: Absorption of Methylene blue mixed with different amounts of NaBiO3 nanoparticles

Figure 3-3 shows the decrease in absorption as time progressed. To study the effect of reaction time, NaBiO3 nanoparticles concentration which showed the highest decrease in the absorption is added to the methylene blue. As shown in Figure 3-3, the intensity of absorption peak decrease consistently with elapsed time. There was a more noticeable difference in the first two hours, and then the degradation slowed down but continued for the full five hours. Immediately after mixing, the sample appeared to be the same color as methylene blue with no nanoparticles. After five hours the samples appeared to be clear.

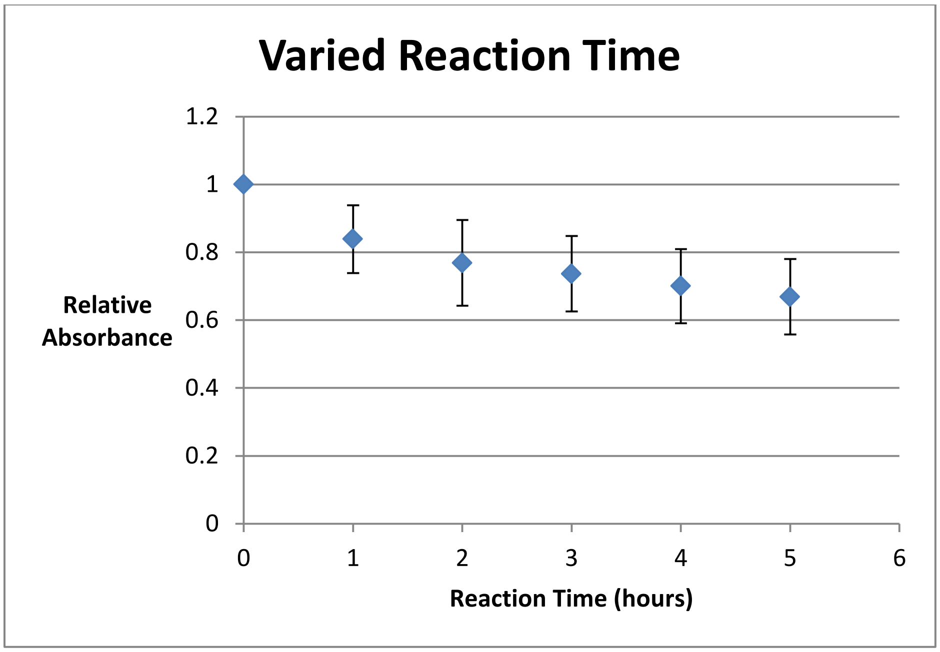

Figure 3-3: Methylene blue mixed with .4 ml $NaBiO_3$ nanoparticles measured immediately after mixing and every hour for five hours.

Figures 3-4, 3-5, and 3-6 show how microwaves affected three different concentrations of nanoparticles. As you can see, the absorbance of each microwaved sample was within statistical error of the control sample no matter the concentration of nanoparticles. There were also no significant changes in the visible color of the samples based on microwave time. The samples with more nanoparticles were still lighter than those with fewer nanoparticles. The microwave irradiation did not stop the nanoparticles from being activated by the natural room light, but did not enhance the photocatalytic abilities of the nanoparticles. Unfortunately, the effects of microwaves did not make a significant difference in the absorption of the solution. Therefore, sodium bismuth oxide nanoparticles are not activated by microwaves and will not work well for MIPDT.

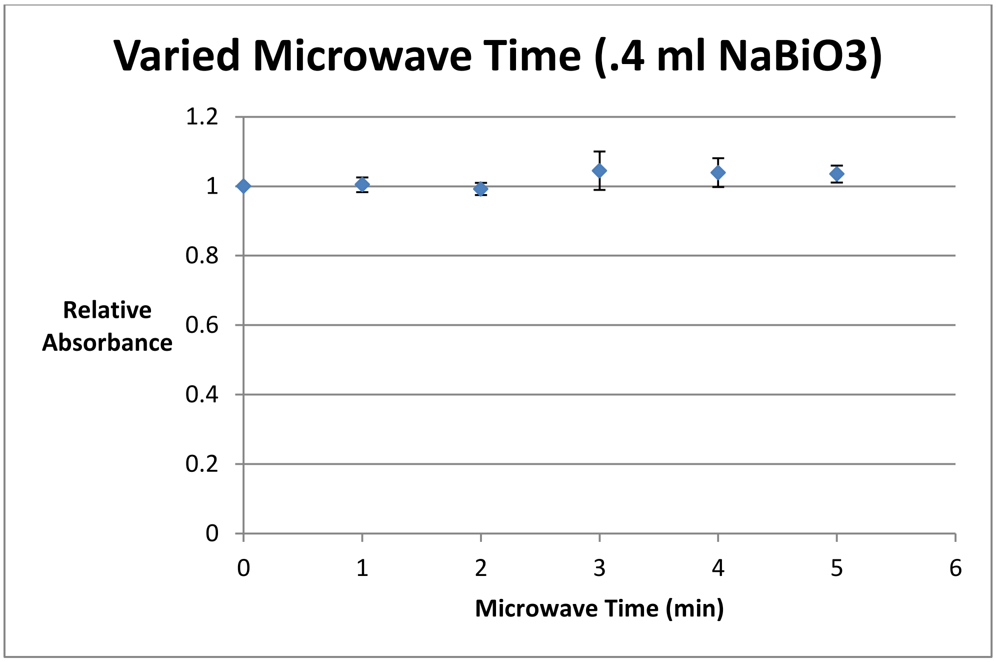

Figure 3-4: Methylene blue mixed with .4 ml of NaBiO3. Each sample was microwaved for 0-5 minutes.

Figure 3-4 shows the highest concentration of nanoparticles used in this experiment. All of these samples were degraded to the point of being clear, but the microwaves had not effect. Each sample was the same color and only had insignificant differences in absorbance.

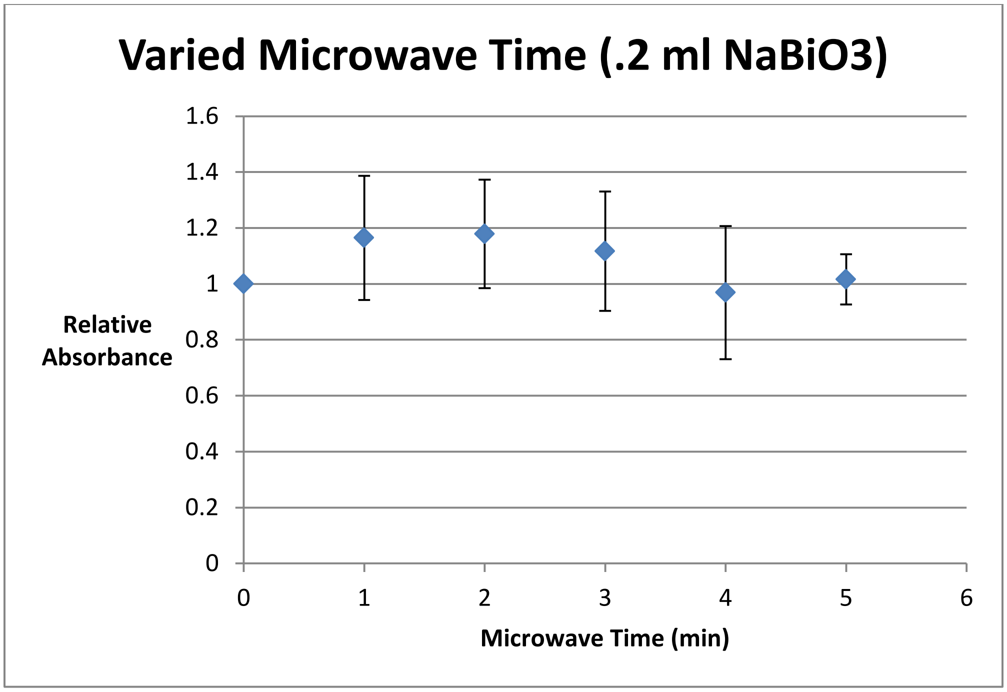

Figure 3-5: Methylene blue with .2 ml NaBiO3. Each sample was microwaved for 0-5 minutes.

The samples involved in Figure 3-5 were bluer than those in Figure 3-4, but there was still no trend caused by the microwave irradiation. All samples with the same concentration had the same visible color and approximately the same absorbance.

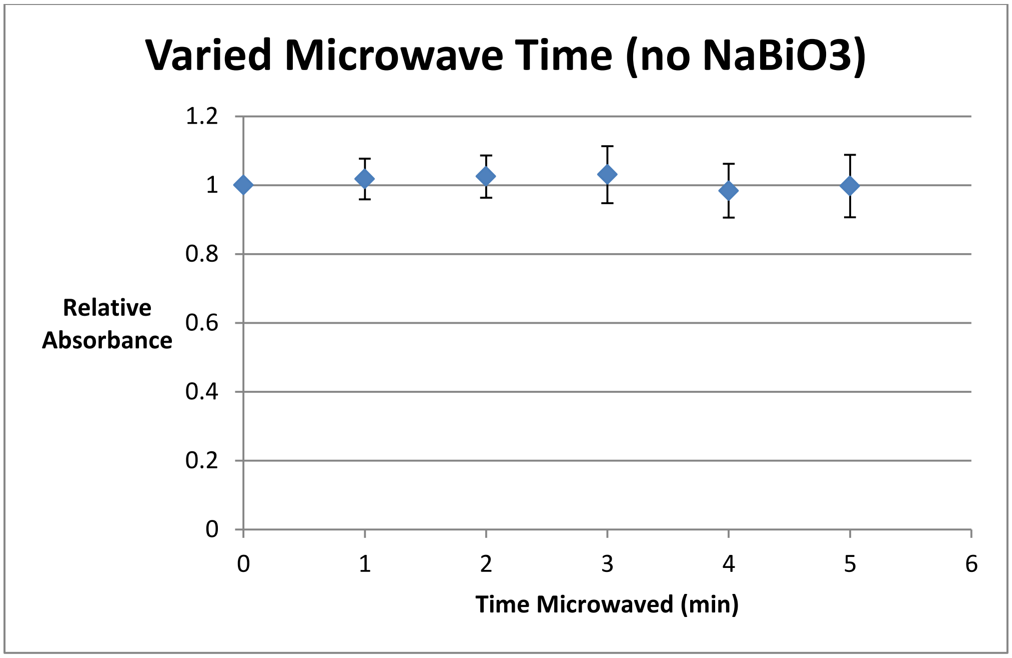

Figure 3-6: Methylene blue with no nanoparticles. Each sample was microwaved for 0-5 minutes.

Figure 3-6 shows that microwaves have no effect on the color of methylene blue alone with no nanoparticles. Therefore, the microwaves had no effect on any of the components of the samples. Each sample was simply heated by the microwave with no significant change in color or absorbance.

Chapter 4

CONCLUSION

Sodium Bismuth Oxide nanoparticles are effective in degrading methylene blue. As the concentration of nanoparticles is increased, the absorption is decreased. The decrease in the absorption of methylene blue due to the addition of nanoparticles shows photocatalyst activity of NaBiO3 nanoparticles. Most of the degradation takes place in the first two hours after the nanoparticles are mixed with the methylene blue. After that, the reaction continues at a slower pace for a few more hours. Microwaves did not have a significant effect on the nanoparticles. The different concentrations of nanoparticles still had the same effect on the methylene blue whether or not they were microwaved. This means that $NaBiO_3$ nanoparticles are not the best photocatalysts for microwave induced photodynamic therapy, but they are effective visible light activated catalysts.

References

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