The Investigation of Iron Oxide Nanoparticles as a Novelty for Smart Windows

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Smart windows electronically change the way light is transmitted through a medium such as glass. With steadily rising energy costs in the United States, smart windows are an excellent choice to reduce energy consumption. One smart window technology, suspended particle devices (SPDs) via Fe_3O_4 (iron oxide) nanoparticles, has presented itself as a viable option for future window applications. However, there are several issues that must be resolved before this technology can be fully implemented. That is, Fe_3O_4 nanoparticles have a low transmittance (<40%) and particle dispersion is not uniform. Also, at high concentrations of Fe_3O_4 it is very difficult for the nanoparticles to return to their opaque state after being transparent. In this study, we further investigate Fe_3O_4 nanoparticles and develop a (Silica) $SiO_2@Fe_3O_4@$ core-shell nanoparticle. Here, we report that by decreasing the concentration of Fe_3O_4, the transmittance increases. In addition, we achieved better particle uniformity and aggregation. Through looking at SEM (scanning electron microscope) images, we successfully created $Fe_3O_4@SiO_2$ core-shell nanoparticles. Our next step is testing the core-shell reliability.

I. INTRODUCTION

Imagine those scorching summer days where the air conditioning is working harder than ever to keep things cool inside your home or office. How about a bone-chilling winter day where the temperature barely hovers above 32 degrees Fahrenheit? In each of these scenarios conventional glass windows play a vital role in our energy costs because it is a poor insulator that allows heat to pass through easily. The resistivity of glass is roughly several hundred to several thousand times less than that of wood, which is the foundation and insulator in many homes and buildings. Therefore, it is easy to understand why smart windows are a good alternative. The extremely simple idea of electronically changing the way windows transmit and/or reflect electromagnetic radiation has been around for several decades. One example is photosensitive eyeglasses while numerous other types of smart window technologies are beginning to be implemented into our homes and offices.

Though the technology is still far from everyday consumer use, the market for it remains unexploited. As a result the glass and window industry has been steadily introducing smart product technologies. According to Freedonia Group, a business research company, the world market for glass is worth around £20 a year ($30.8 billion US 2013 dollars), with the building industry accounting for roughly half this sum [1]. With the knowledge that windows account for nearly 25 percent (at times much more) of heating and cooling buildings, there is a priority for consumers and contractors to adopt this technology.

This paper presents the feasibility of Fe_3O_4 and $SiO_2@Fe_3O_4$ core-shell nanoparticles as suspended particle devices in smart windows. **Part II** provides a brief Background into the various smart window technologies. Then it will focus on the technology my project explores in particular and the benefits it may bring. **Part III** will discuss the Procedure in detail of creating the nanoparticles and assembling the pixel device. **Part IV** is the Experimental Results section. **Part V** will present Conclusion and Discussion. **Part VI** and **VII** are Acknowledgements and References.

II. BACKGROUND

Smart window technologies include thermochromics, photochromics, polymer dispersed liquid crystals (PDLCs), electrochromics, and suspended particle devices (SPDs). Each technology offers its own unique solution.

A. THERMOCHROMICS

Thermochromic technology change state from transparent to progressively less transparency in response to changes in ambient temperature and light intensity. Polyvinyl butyral (PVB), the most promising thermochromic technology for use in smart windows, is laminated onto glass. As light and heat attempts to enter windows coated with this material, a significant portion of both are absorbed and reflected away. **Fig. 1** shows a schematic of the process. In addition, tinted glass may be used as well to provide a desirable outside appearance for buildings and homes.
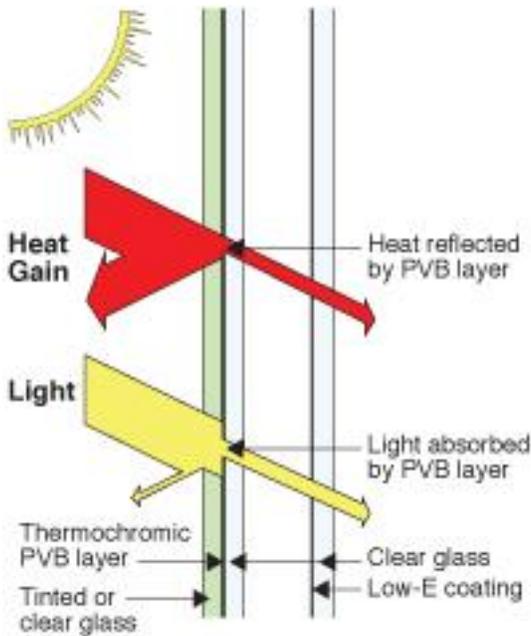
Figure 1. "Windows for high-performance commercial buildings" PVB thermochromic window

B. PHOTOCHROMICS

Photochromic technology operates in response to light. For, example as light penetrates through a window with photochromic technology, the window darkens and light transmission decreases. While this type of technology appears to be a good choice, it is ultimately impractical as an energy saving device. It regulates heat flow very poorly because the amount of light that strikes a window doesn't necessarily correlate to the amount of solar energy it absorbs. For example during the winter months when the sun is lower in the sky, solar rays may strike a window more intensely than during the summer. As a result, a photochromic window would darken more in the winter than in the summer, although winter is the time when solar heat would be beneficial.

C. POLYMER DISPERSED LIQUID CRYSTALS

In PDLCs liquid crystals are suspended randomly between two panes of glass with conductive coatings on each side facing the other. When a voltage is applied to the glass the liquid crystals respond by aligning to the same plane the light passes through. In other words, the angle between the liquid crystals and light is zero. When the voltage is removed the crystals go back to their random positioning. **Fig. 2** shows a schematic of how PDLCs works. It is conveniently dubbed "privacy glass" because in the off state while light still passes through, the information is scrambled. The result is a very foggy image. The main drawback in PDLCs is that there are only two modes of operation, transparent or opaque [2,5].
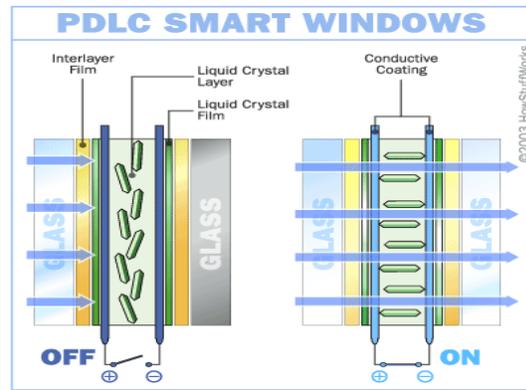
Figure 2. "How Smart Windows Work" PDLC smart window in its on and off state

D. ELECTROCHROMICS

Electrochromics materials change color when energized by an electric field. This technology consists of a conductive, ion storage, and electrochromic layer between two panes of glass. The electrochromic layer is an ion-conducting film such as tungsten oxide (WO_3). The ion storage reservoir for example, is lithium ions (Li^+). When the electric field is applied the lithium ions move from the reservoir to the electrochromic material and react to produce $LiWO_3$. The chemical reaction that takes place changes the device from non-light absorbing (transparent) to light absorbing with a specific wavelength of light reflected characteristic of $LiWO_3$. It is this reflected wavelength that we see as the color of the device. The reaction is reversible and a constant voltage is not required to sustain it. A voltage is only required to change its initial conditions. Usually electrochromic materials only have a maximum of two colors associated. **Figs. 3 and 4** show a schematic of an electrochromic device [1,3,4,5].
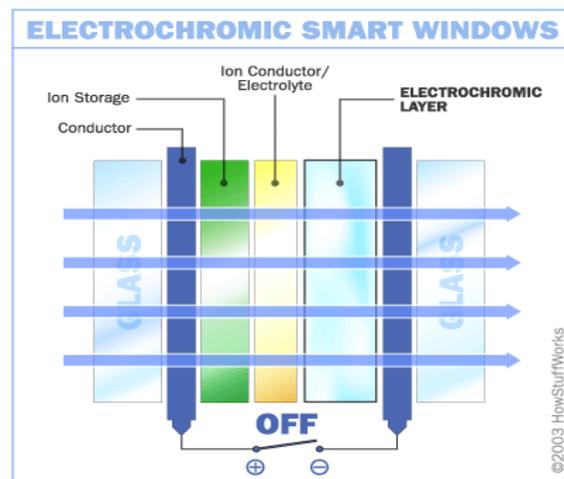
Figure 3."How Smart Windows Work" Off state of electrochromic device
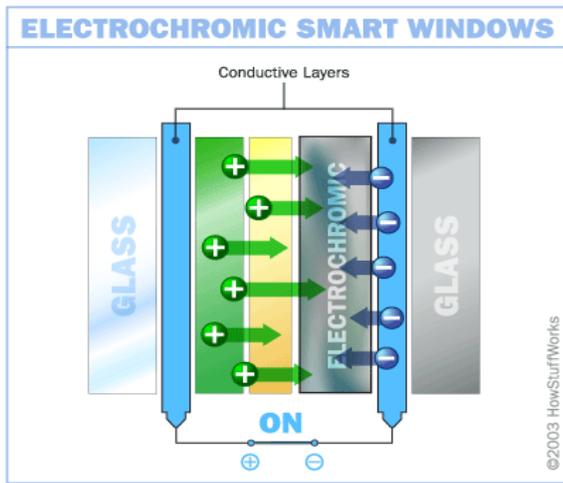
Figure 4. "How Smart Windows Work" On state of electrochromic device

E. SUSPENDED PARTICLE DEVICES

The functionality behind SPD technology is that it absorbs light transmission by the random alignment microscopic particles are suspended in when there is no voltage. These particles are suspended between two glass substrates with conductive coatings on each side. When a voltage is applied across these substrates the particles align as a set and light passes through. A signal of alternate voltage with different amplitudes can align more or less efficiently the particles depending on the effective voltage of the applied signal [6]. **Fig. 5** shows a schematic of an SPD device.
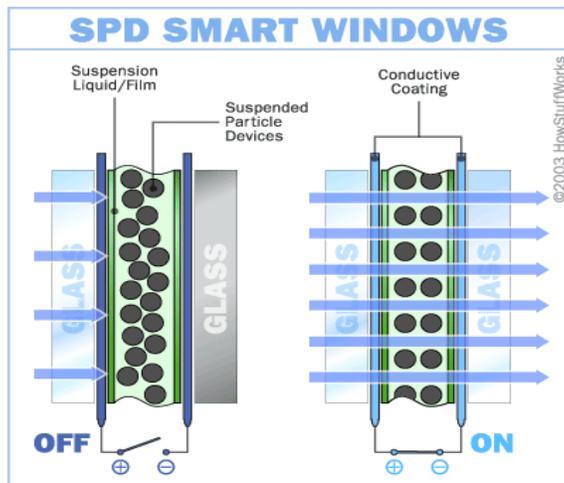
Figure 5. "How Smart Windows Work" SPD in on and off state

Although thermochromics, photochromics, PDLCs, and electrochromics reduce light transmission, all lack the colorful characteristics SPDs have. What I mean by this is that we believe our technology should also provide a beautifully colored surrounding to our consumers. Consumers would be ecstatic to acquire a window that is very pretty, colorful, and reduces light transmission. The colorful characteristic that SPDs have is the reason why my project has focused on this type of technology in particular. We believe that by using

Fe_3O_4 and $SiO_2@Fe_3O_4$ core-shell nanoparticles as the particle in SPDs smart windows, colorful smart windows can be produced.

III. EXPERIMENTAL PROCEDURE

A. FE₃O₄ NANOPARTICLE FABRICATION

Ferrocene ($Fe(C_5H_5)_2$), hydrogen peroxide (H_2O_2), and acetone (C_3H_6O) were obtained and used as received without further purification. Ferrocene (0.3g) was added to 22ml/30g of acetone and ultrasonic bath for 1 minute to ensure particle dispersion. Next, 1.5ml of H_2O_2 was added to the solution. The solution was then transferred to a Teflon-lined enclosure and afterwards an autoclave enclosure. The contents were heated at 200 degrees Celsius for 48 hours. The chemical reaction that takes place creates the Fe_3O_4 nanoparticles. **Fig.6** shows the process. **Fig. 7** shows a scanning electron microscope (SEM) image depicting what we expect the Fe_3O_4 nanoparticles to look like.
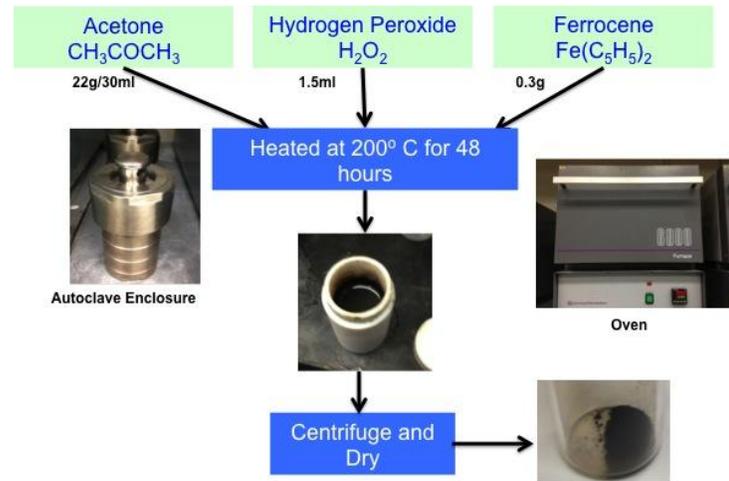
Figure 6. Fe₃O₄ nanoparticles fabrication process
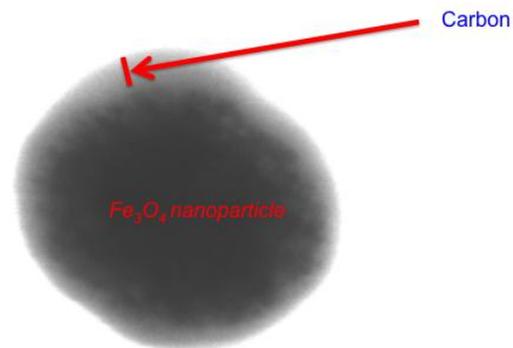
Figure 7. Scanning electron microscope (SEM) image of Fe₃O₄ nanoparticle in a carbon shell. During the heating process, carbon forms (light grey color) a shell around the Fe₃O₄ nanoparticles. This combines the individually smaller Fe₃O₄ nanoparticles (dark color) into a bigger particle shown.

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B. SIO$_2$@FE$_3$O$_4$ CORE-SHELL NANOPARTICLE FABRICATION

These nanoparticles were prepared following the same procedure in **section A.** The slight difference is that 0.1g of silica was added and the amount of ferrocene added each time varied. **Fig. 8** shows the process and **Fig. 9** shows a SEM image confirming that SiO$_2$@Fe$_3$O$_4$ core-shell nanoparticles were successfully fabricated.
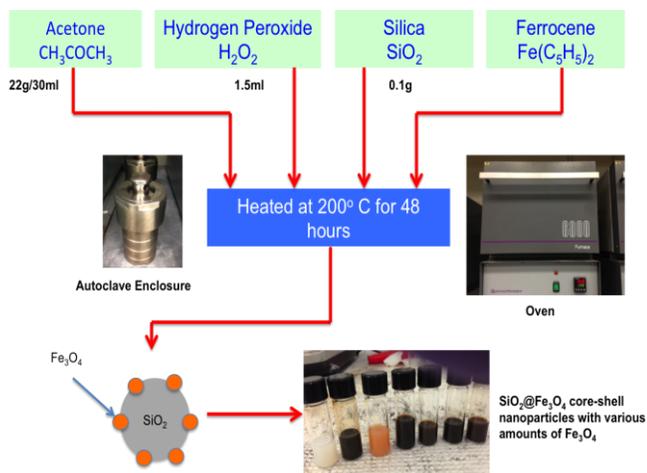
Figure 8. SiO$_2$@Fe$_3$O$_4$ core-shell nanoparticle fabrication process
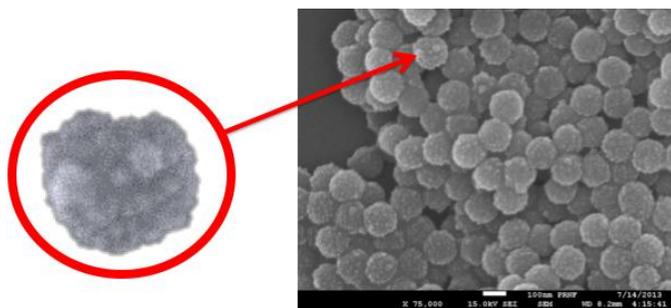
Figure 9. SEM image of SiO$_2$@Fe$_3$O$_4$ core-shell nanoparticle. In the circled zoom-in image part, the lighter shading is Fe$_3$O$_4$ nanoparticles while the darker shading is the SiO$_2$ nanoparticle.

C. PURIFICATION

Fe$_3$O$_4$ and SiO$_2$@Fe$_3$O$_4$ core-shell nanoparticles followed the same procedure in this section and **section D**. After the nanoparticles were removed from the oven, they were allowed to cool for 2 hours. Using a pipet, the contents were transferred to two 50ml centrifuge tubes. The tubes were centrifuge at 6500 rpm for 15 minutes. At the end of the cycle extraneous fluids containing any excess ferrocene were dumped in a waste container. This left only a little liquid remaining containing the nanoparticles. Acetone was added to

the 15-20ml mark of the tube and centrifuge again under the same conditions. This process of centrifuge and dumping extraneous fluids was typically performed at least 3 times to ensure that any remaining ferrocene was removed. Once centrifugation was complete the nanoparticles were left to dry for 1-2 days under a fume hood.

D. CREATING THE FINAL SOLUTION

The mass of the nanoparticles was recorded and transferred to a small vial. The vial was filled with acetone to the halfway mark and placed in an ultrasonic bath to uniformly disperse the particles for 2 hours. Propylene carbonate (PC) was injected into each vial of solution. The amount of PC each vial received was determined by equation (1).

$$PC = \frac{(mass\ of\ nanoparticles)}{42.86} \times 100 \quad (1)$$

The nanoparticles were placed in the oven for 6 hours at 65 degrees Celsius for the acetone to evaporate. **Figs. 10 and 11** show Fe$_3$O$_4$ and SiO$_2$@Fe$_3$O$_4$ core-shell nanoparticles injected with PC. In **Fig. 11**, the arrow shown describes the decreasing amounts of ferrocene added to fabricate the Fe$_3$O$_4$ nanoparticles present in the core-shell solution.
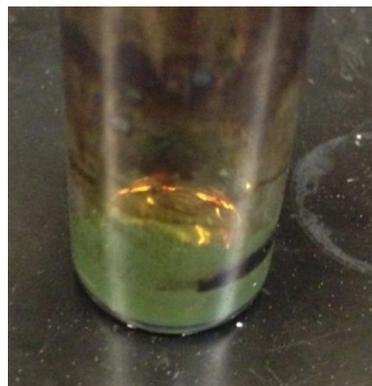
Figure 10. Fe$_3$O$_4$ nanoparticles in PC solution
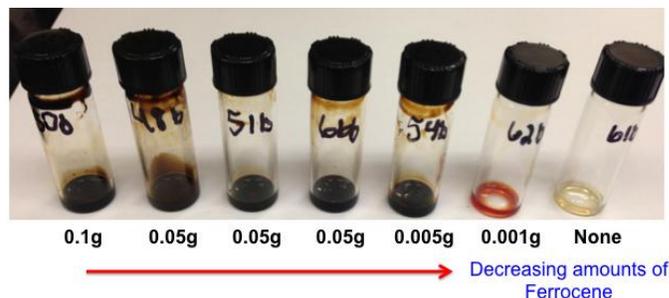
Figure 11. SiO$_2$@Fe$_3$O$_4$ nanoparticles in PC solution

E. PIXEL ASSEMBLY

Two pieces of 2x2 inch Indium Tin Oxide glass were retrieved and cleaned with acetone and isopropanol alcohol. An ohmmeter was used to test the glass to find its conductive side. The conductive sides were placed facing each other. A 25-micrometer thick film spacer of polyethylene terephthalate (PET) was placed in between the two conductive sides leaving a 3mm hole on each side. **Figs. 12 and 13** show a schematic of this process.
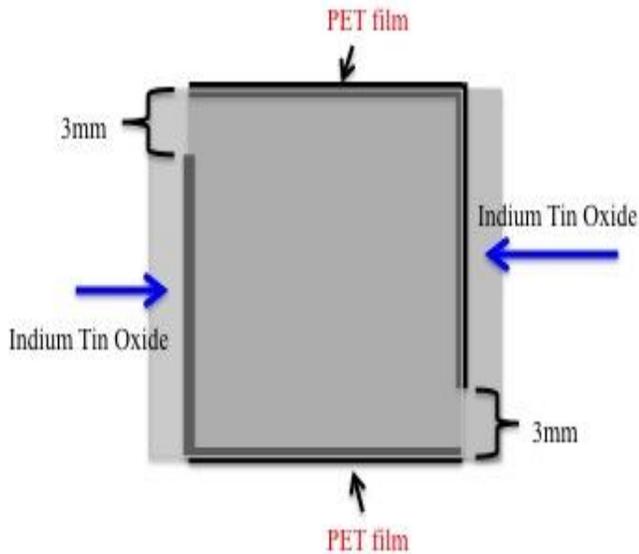
Figure 12. Overhead view of ITO pixel
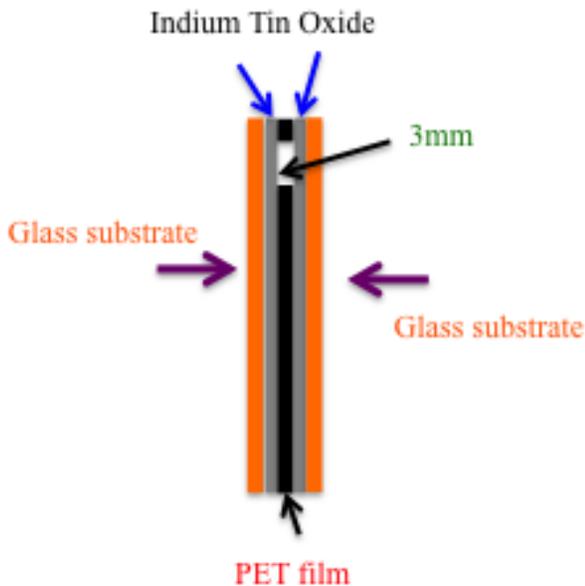
Figure 13. Side view of ITO pixel

The empty pixel was held into place by clamping down two of its sides. Epoxy glue, which takes about 5 minutes to bond,

sealed the edges of the pixel and the clamps were removed. Metal contacts using a thin 4x4 mm copper sheet were attached to both sides of each pixel where the 3mm gap is located. Finally, a silver solder paste gently applied bonded a metal wire onto both copper contacts.

The Fe_3O_4 nanoparticle solution was inserted into the 3mm gap of each pixel using a 100ml micropipette with a total capacity of 1ml per injection. Simultaneously, a vacuum tube was attached to the opposite gap helped spread the solution uniformly across the pixel.

IV. EXPERIMENTAL RESULTS

Morphologies of our nanoparticles were investigated using a Field-Emission high-resolution scanning electron microscope (JEOL 7500F SEM) operating at 20kV. The optical characteristics of the pixel device were analyzed using a Varian Cary 5000 Spectrophotometer. **Fig. 14** displays a graph of transmittance vs. wavelength taken by the spectrophotometer at concentrations of 25%, 17.5%, and 7% Fe_3O_4. As the concentration in **Fig 14** decreases there is an increase in transmittance. This means that our device becomes more transparent. **Fig. 15** shows a graph of transmittance vs. wavelength at different voltages. The primary goal of **Fig. 15** is to show that as the voltage increases transmittance increases. However, this is only partially correct. As **Fig. 15** shows, beyond 5V transmission began decreasing. We found that above 5V the Fe_3O_4 nanoparticles may become unstable and revert back to its opaque state. At voltages typically below 2V the transparency of the device does not change. Instead, the color changes. **Fig. 16** shows the Fe_3O_4 pixel device color change at 0V to 2V. **Figs. 17, 18, and 19** show the pixel device at 0V, 5V, and 10V.
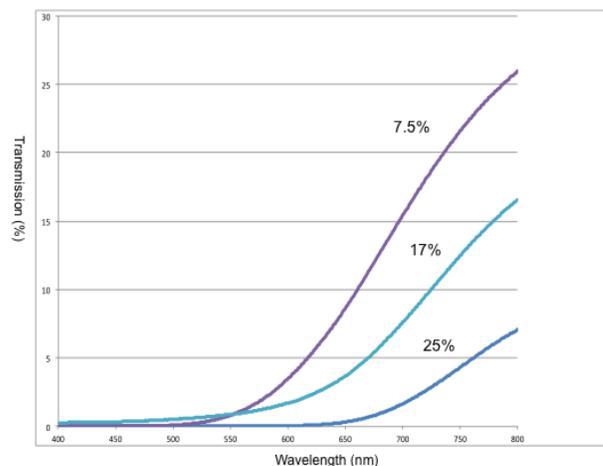
Figure 14. Transmission vs. wavelength of Fe_3O_4 nanoparticle device at various concentrations
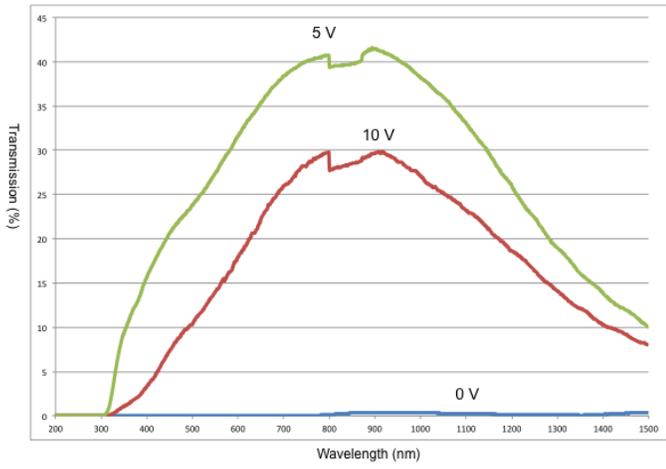
Figure 15. Transmission vs. wavelength of Fe_3O_4 nanoparticle device at different voltages

Figure 17. Fe_3O_4 nanoparticle pixel at 0V
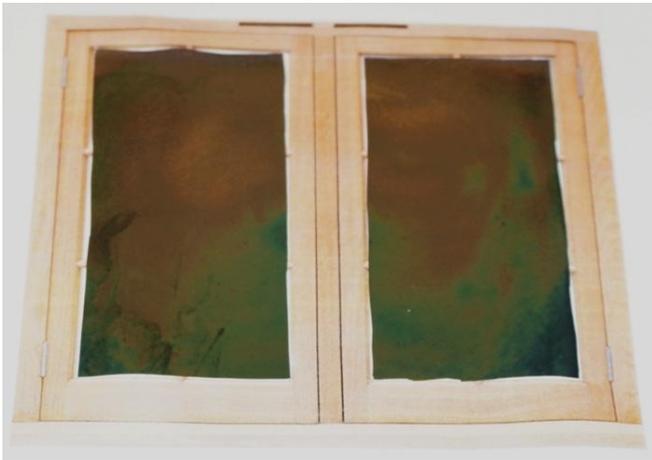
Figure 16. Fe_3O_4 nanoparticle pixel modulated at 0V to 2V

Figure 18. Fe_3O_4 nanoparticle pixel at 5V

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Figure 19. Fe_3O_4 nanoparticle pixel at 10V

V. DISCUSSION AND CONCLUSION

Throughout the process of purification and solution creation of Fe_3O_4 and $SiO_2@Fe_3O_4$ core-shell nanoparticles we encountered a number of obstacles that affected our results. Some nanoparticles were lost in the waste container after we disposed of the excess fluids remaining in the samples. As the nanoparticles were ultrasonic bath to disperse in acetone for PC solution preparation, some failed to disperse completely. We also encountered leakage in the Fe_3O_4 pixel devices. A probable cause is that we didn't completely seal the device in epoxy and there are very small holes in the device. In **Figs. 8 and 11** there is a sample of $SiO_2@Fe_3O_4$ core-shell nanoparticles that has an orange color. We believe that since that particular sample had such a low amount of ferrocene present to create Fe_3O_4 nanoparticles, some formed Fe_2O_3 nanoparticles as well. Fe_2O_4 has a reddish color which would give the sample in **Figs. 8 and 11** its orange color.

In conclusion, we fabricated Fe_3O_4 and $SiO_2@Fe_3O_4$ core-shell nanoparticles. We assembled the pixel device and injected it with Fe_3O_4 nanoparticles. The device optical characteristics were analyzed by a spectrophotometer. The results found show that as the concentration of Fe_3O_4 nanoparticles decreased, transmittance increased. Nevertheless, more work need to be completed. Future work involves further reducing Fe_3O_4 concentration and trying various solvents other than propylene carbonate. In addition, we want to insert the $SiO_2@Fe_3O_4$ core-shell nanoparticles into the pixel device and test its optical characteristics.

VI. ACKNOWLEDGEMENTS

VII. REFERENCES

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