

Electrochromic Adaptive Infrared Camouflage

Interim Progress Report

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13. ABSTRACT (Maximum 200 words) The goal of this research program was to create a technology for artificially programmable infrared emissivity of surfaces. As an example, this would permit a vehicle, or a person to blend into its surroundings, and become invisible to an infrared camera. A great deal has been accomplished in this research program, that will help convert this technology into a practical reality. The main technical objective is the controlled reduction of infrared emissivity. An emissivity reduction not an increase is desired, since objects of interest are generally hotter than their surroundings. The tunability of emissivity is made possible by electrochromics. Today, electrochromics is becoming a common technology that is used, for example, in self-dimming rear view mirrors in automobiles. Electrochromic materials change their color by undergoing an electronic transition of some form. In the most common type the electronic transformation is induced electro-chemically in special polymeric materials. In effect this is a type of electrochemical doping, with the material thereby undergoing a transition from an insulator to a metal, with the corresponding changes in color.				
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Final Report on
ELECTROCHROMIC ADAPTIVE INFRARED CAMOUFLAGE MURI

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Principal Investigator: Prof. **Eli Yablonovitch**
Co-P. I: Prof. **Fred Wudl**
Co-P. I. Prof. **Bruce Dunn**

University of Florida:
Co-P. I: Prof. **John R. Reynolds**
Co-P. I: Prof. **David B. Tanner**

with additional participation by
Prof. **Ray H. Baughman** & Prof. **Anvar A. Zakhidov**, Univ. of Texas, Dallas

EXECUTIVE SUMMARY:

The major accomplishments of this research program were as follows:

1. We fabricated and tested the first inverse opal infrared “white” pigment.
2. We made the first electrochromic cell that operated in the important 8 μ m-12 μ m atmospheric transmission window.
3. We made the first all-polymer electrochromic cell, that contained no metallic components.
4. We achieved 80% contrast, electrically tuned, in an infrared electrochromic cell.
5. We demonstrated electrochromic switching in 67 milli-seconds, essentially a video rate.

INTRODUCTION:

The goal of this research program was to create a technology for artificially programmable infrared emissivity of surfaces. As an example, this would permit a vehicle, or a person to blend into its surroundings, and become invisible to an infrared camera. A great deal has been accomplished in this research program, that will help convert this technology into a practical reality.

The main technical objective is the controlled reduction of infrared emissivity. An emissivity reduction not an increase is desired, since objects of interest are generally hotter than their surroundings. The tunability of emissivity is made possible by electrochromics. Today, electrochromics is becoming a common technology that is used, for example, in self-dimming rear view mirrors in automobiles. Electrochromic materials change their color by undergoing an electronic transition of some form. In the most common type the electronic transformation is induced electro-chemically in special polymeric materials. In effect this is a type of electrochemical doping, with the material thereby undergoing a transition from an insulator to a metal, with the corresponding changes in color.

There are two possible approaches to emissivity control:

- (a) It is possible to imagine that the electronic transition is to a metallic state, that might have high reflectivity.
- (b) The insulating state would be transparent, and it could be backed up by a highly reflective medium.

It turns out that the first option, (a) using the electrochemically doped metallic state as a reflector is not practical. The electro-chemically doped metals are actually not very good reflectors in the infrared. The materials are still somewhat resistive, compared to conventional metals, and therefore they are actually good absorbers in the infrared, rather than good reflectors. This is illustrated in Figure 1. The visible band and infrared band have surprisingly opposite behaviour. Therefore we employed option (b) above.

The requirements then were a polymeric material that was relatively transparent in the undoped state, and an infrared pigment that was “white” in the infrared. Such an infrared pigment would represent new technology, made for example by inverse opal photonic crystal particles in which short range order would suffice. Such an infrared pigment would coat the rear side of the

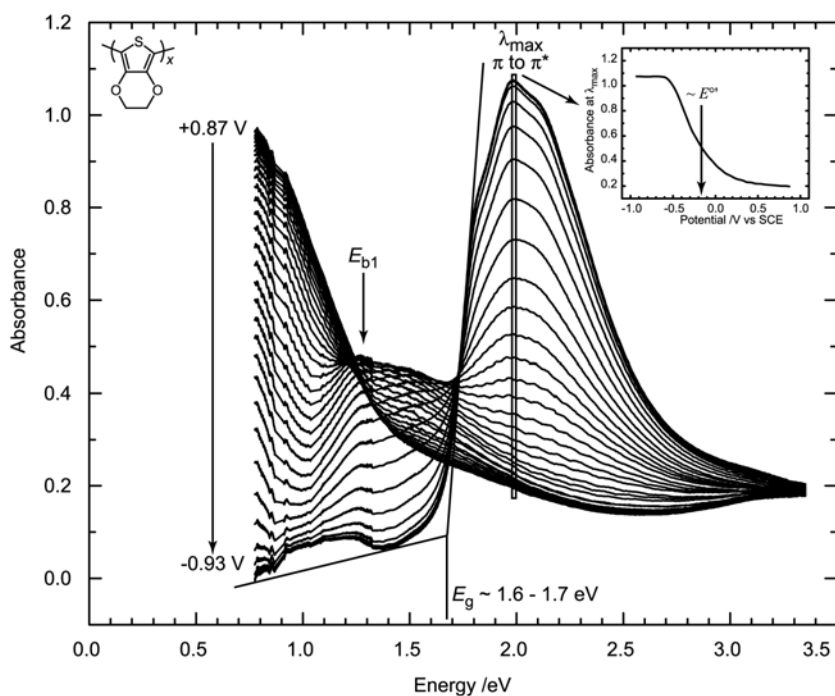


Figure 1: The absorbance of PEDOT in the visible and the infrared. Notice the counter-intuitive effects of doping. Doping eliminates the strong absorption in the visible, but the added carriers increase the absorption in the infrared.

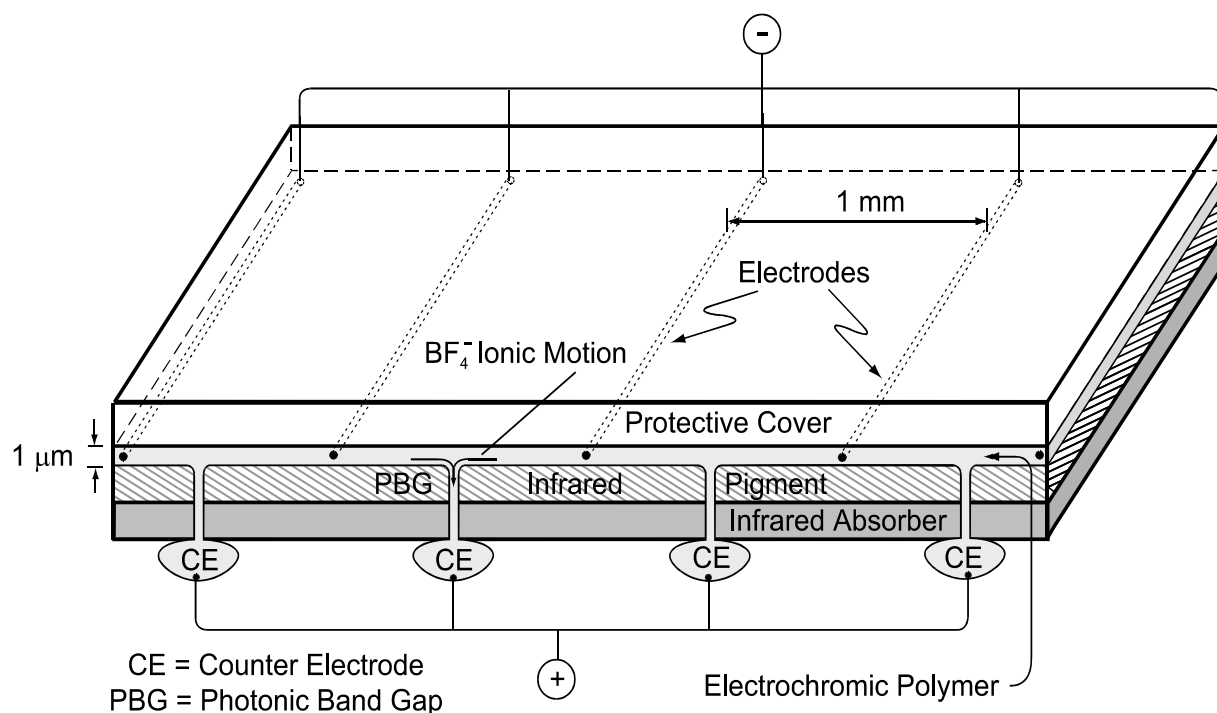


Figure 2: The basic strategy for controlling infrared emissivity by means of an electrochromic cell.

electrochromic polymer, as shown in Figure 2. Such an infrared pigment could be regarded as a superior form of “white” pigment compared to titanium dioxide particles that are commonly used as white pigments in the visible range.

Thus the work divided itself into two parts:

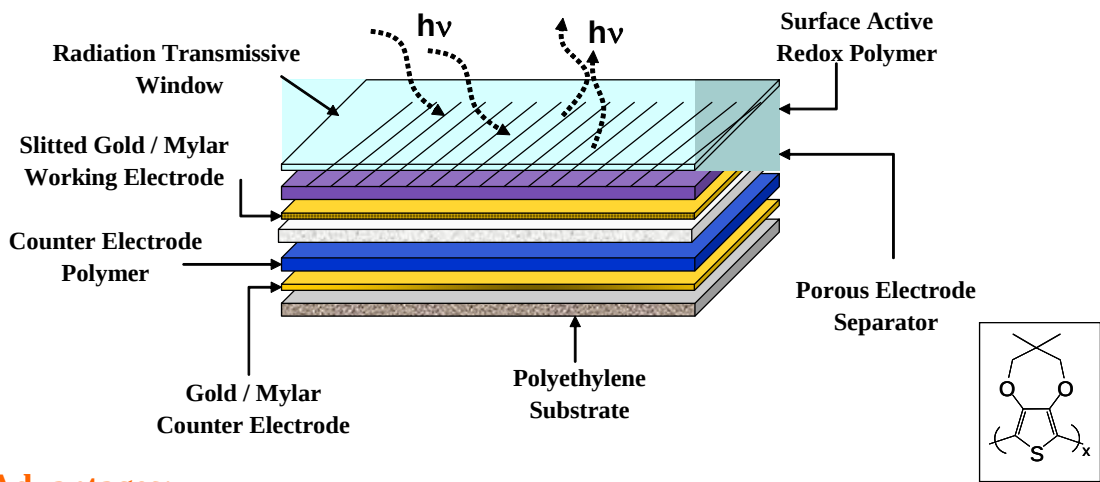
- (1) The construction of the infrared electro-chemical cell with the highest infrared contrast possible.
- (2) The fabrication of this new type of infrared pigment based on a powder made of inverse opal photonic crystals. It made sense to build the inverse opal photonic crystals out of chalcogenide glasses, that had the required infrared transparency, and the desirable high refractive index.

Most of the team’s effort (Reynolds, Tanner, Wudl, and Dunn) was directed toward the difficult task of building the infrared electrochemical cell, with the Principal Investigator directly supervising the infrared opal work that was taking place in the laboratory of Ray Baughmann. Initially that work was in the industrial AlliedSignal lab that had considerable experience with pigments as part of their textile business. During this MURI program, there were a number of mergers, and corporate changes, and the Baughmann/Zakhidov team moved their research lab to the Univ. of Texas, Dallas. With minor disruptions they continued their progress toward infrared chalcogenide photonic crystal reflectors until the completion of this MURI program.

FABRICATION OF THE INFRARED ELECTROCHROMIC ELECTROCHEMICAL CELL:

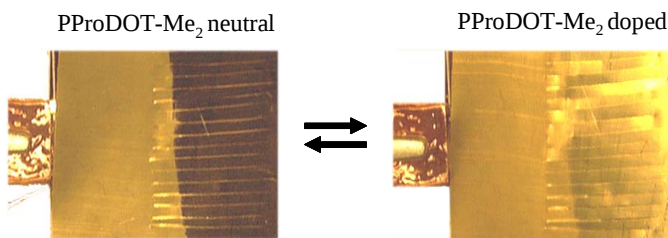
Responsibility for the creation of the infrared electrochemical cell fell to Reynolds and to Dunn, who had parallel approaches. Wudl concentrated on the synthesis of novel narrow bandgap electrochromic polymers, that would have more specialized applications, like the fine tuning of the infrared response over a particular narrow portion of the infrared..

Figure 3: A very successful infrared electrochromic cell fabricated by our Florida group. In this case, the reflective pigment behind the Redox polymer is actually a slitted reflective gold film, rather than the inverse opal chalcogenide photonic crystal that is one of the goals of the program. All the layers below the slitted gold film are simply for the purpose of providing a practical counter-electrode for the active Redox polymer.



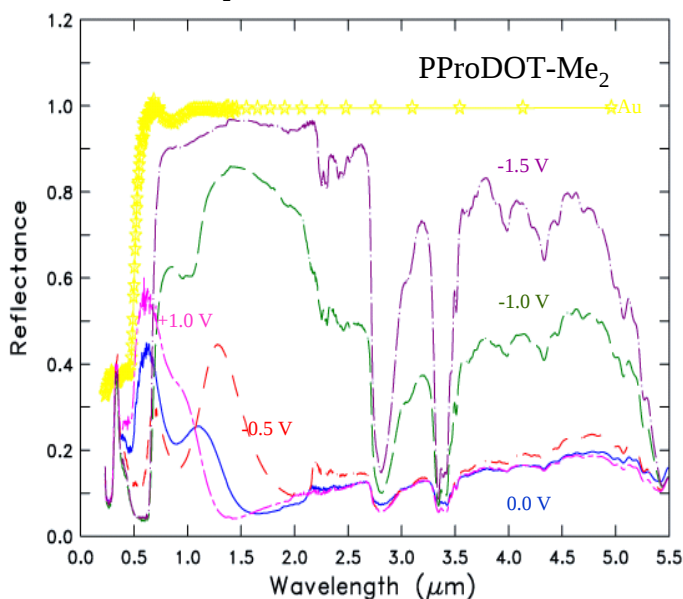
Advantages:

- top window can be chosen to be highly transmissive over the region of interest
- flexible
- air free by encapsulation



The preferred dopable polymer for these infrared electrochromic was generally PEDOT-Me₂ whose structure is illustrated in the inset to Figure 3. Nevertheless, a wide variety of candidate polymers were investigated.

The infrared performance allows for over 80% emissivity contrast as shown in Figure 4.



- Observation of the electronic transitions characteristic of the neutral (π - π^*), intermediate doped (polaronic) and heavily doped (bipolaronic) states.
- $\Delta\%R \sim 80\%$ in the 1.2 – 2.5 μm region.
- $\Delta\%R \sim 50\text{--}60\%$ in the 3.5 – 5.0 μm region.
- Substrates:
Glass $\rightarrow$ low wavelengths.
ZnSe $\rightarrow$ high wavelengths.
- Two strong absorption bands:
O-H (water) at 2.7 μm and
C-H stretching at 3.3 μm .

Figure 4: Tuning the infrared emissivity, electrochemically. 80% contrast is achieved.

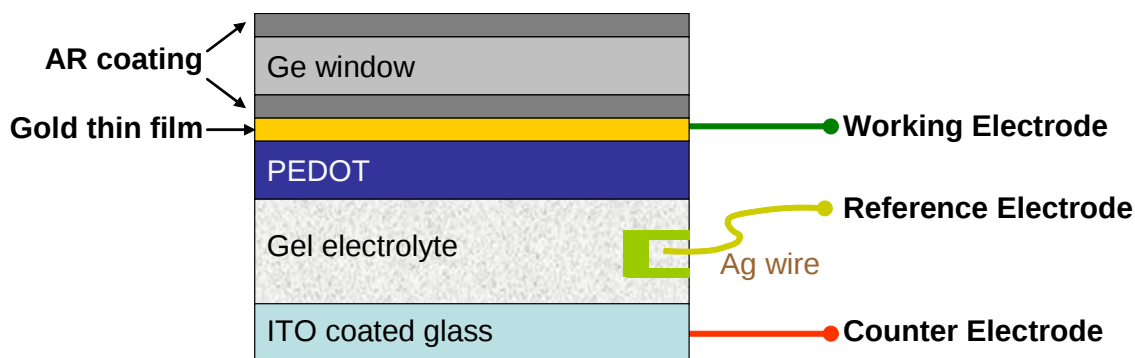


Figure 5: This electrochemical design permitted emissivity modulation in the 8 μ m-12 μ m atmospheric window.

Such a high contrast level bodes well for the practical application of this technology in the field. Nonetheless, a cursory examination of Figure 4, shows strong absorption peaks at the water band, and in the CH stretching band, where there is weak modulation contrast. The water peak can be removed by careful drying of the polymer, and the CH stretch can be diminished to about a 20% peak, that still permits considerable modulation. The contrast seems to peak for an electrochromic polymer film thickness, <400nm.

In tests, after 10,000 deep double switches the polymer was still electrochemically very active, with only a 12% loss in reflectance difference. By substituting a commercially available PMMA porous white membrane, (that is supposed to emulate our inverse opal infrared pigment), in place of the slitted gold film reflector, the path that the ions had to follow was greatly shortened. This allowed the resistive drop to diminish and permitted faster switching times, <1sec. Starting from 74% contrast, after 168,000 cycles the contrast had only dropped to 66%, at an infrared wavelength of $\lambda=1.5\mu$ m.

Furthermore Dunn has also studied mesoporous electrode configurations that allow for even faster reduction and oxidation of the electrochromic polymer. Switching times as fast as 67milli-sec was observed, which is close to video rates.

There were also experiments in which the counter electrode was also an electrochromic polymer. This allowed for novel architectures in which various double sided effects could be demonstrated. These “metal-free” electrochromic cells are expected to be useful, where metal electrodes could cause difficulties.

The electrochromic cell experiments were extended well into the 8 μ m-12 μ m atmospheric window. The cell geometry is shown in Figure 5. The new features included a proper Germanium window, anti-reflection coated. Excellent reflection contrast is noted in Figure 6,

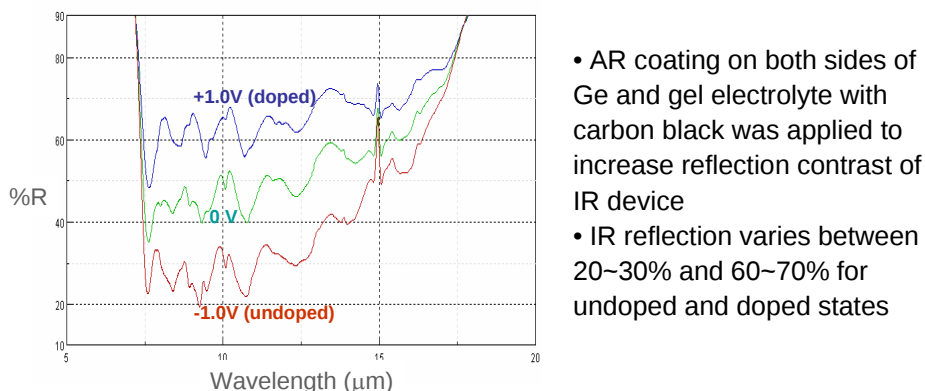


Figure 6. Significant reflection modulation in the 8 μ m-12 μ m atmospheric window. Contrary to previous cases, the performance improved with carbon black impregnated absorbing gel electrolyte, rather than the “white” pigment electrolyte.

although using a black reflector, rather than a white reflector. Owing to the relatively permeable PMMA-based gel electrolyte, switching times <100milli-sec were observed again.

The results presented above represent a number of firsts, that we are proud of, including:

1. We made the first electrochromic cell that operated in the important 8 μ m-12 μ m atmospheric transmission window.
2. We made the first all-polymer electrochromic cell, that contained no metallic components.
3. We achieved 80% contrast, electrically tuned, in an infrared electrochromic cell.
4. We demonstrated electrochromic switching in 67 milli-seconds, essentially a video rate.

This level of electrochromic cell performance should be very suggestive to government decision makers who are interested in the potential of electrochromics for emissivity control. None of the electrochromic cells listed above took advantage of the inverse opal infrared pigment structures, that were being developed at the University of Texas. Those novel pigments are expected to produce even higher levels of performance.

SYNTHESIS OF LOW BANDGAP INFRARED ELECTROCHROMIC POLYMERS:

Prof. Fred Wudl took the lead in this project. Such low bandgap infrared polymers could be very useful in fine-tuning infrared response, within an electrochemical cell that is oriented toward overall reduced emissivity. Wudl was able to produce polymers with a bandgap as small as 0.2electron-Volts. His strategy was to combine a molecular group with a low energy Lowest Unoccupied Molecular Orbital, (LUMO) with another group with a relatively high, Highest Occupied Molecular Orbital, (HOMO). This squeezed the electron transition energy splitting to make it low enough to be useful in the infrared.

An example of such a low bandgap polymer is shown in Figure 7.

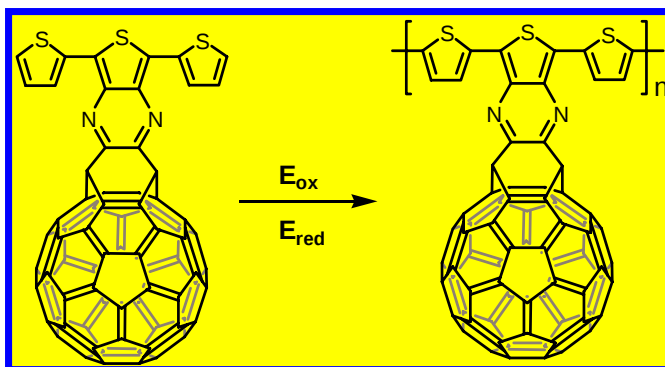


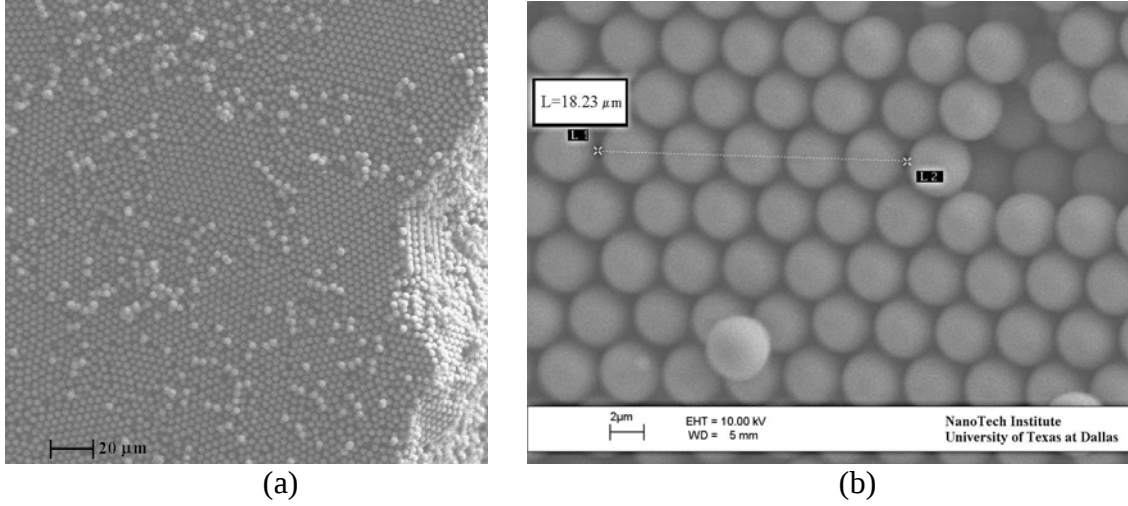
Figure 7: These unusually large groups attached to a polymeric backbone, results in very low infrared bandgap electrochromic polymers.

FABRICATION OF INFRARED WHITE PIGMENT:

In general the infrared electrochromic cells should perform best with a white pigment backing. When the polymer is undoped, it transmits radiation that is reflected by the white backing, resulting in a low emissivity. Conversely, when doped, the polymer is quite absorbing in the infrared, (though not in the visible). Usually the polymer is thin enough, <400nm, that the infrared vibrational bands in the polymer itself have small effect, but that thickness is more than enough to hold a sufficient density of doped electrons per square centimeter to be strongly absorbing. Thus the goal of tunable low emissivity relies on having a low emissivity backing on the undoped polymer. The work described below was done by Dr. Ali Aliev working at the Univ. of Texas, Dallas.

We have chosen to work with the chalcogenide glasses that have bandgaps compatible with infrared transmission, are easy to fabricate, and have among the high refractive indices known. The high refractive index insures strong scattering which produces the lowest possible

Figure 8: SEM image of a sintered opal template fabricated from silica microspheres of 3.9 μm . (a) Low-magnification image showing long-range ordering. Several ordered layers can be seen on the fractured edge to the bottom right. (b) High-magnification image showing a slight decrease in the lattice parameter after sintering at 900°C for 24 hours. The average distance between spheres reduced from 3.9 μm to 3.65 μm .



emissivity. Indeed, in the visible region of the spectrum TiO_2 is used as a white pigment for the same reason. It has the highest known refractive index in the visible. In the same way chalcogenides have even higher refractive index, but in the infrared.

There have been numerous studies of inverse opal photonic crystals. Their photonic bandgap is not very wide, but the structure scatters strongly over a broad range of frequencies. The starting point for these strongly scattering structures is a face centered cubic arrangement of polystyrene spheres as shown in Figure 8. Similar SEM pictures have been shown by research groups around the world, but usually at a size scale about 5-10 times smaller, where they are suitable at visible frequencies. We believe that we are the first with such large opal structures whose period is suitable for the infrared. Special care was taken with the purification of these spheres to make certain that non-spherical impurities were removed.

Table I: Properties of some potential opal infiltration materials.

Name	Formula	Refraction index	Transmission range (μm)	Melting point ($^{\circ}\text{C}$)
AMTIR-1*	$\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$	2.514 (4 μm) 2.497 (10 μm)	0.9 - 16	370
Arsenic selenide	As_2Se_3	2.41 (4 μm)	2.0 - 12	260
Arsenic sulfide	As_2S_3	2.41 (5 μm)	1.5 - 8	310
Gallium Arsenide	GaAs	3.3 (4 μm)	1.0 - 15	1238
	$\text{Ge}_{25}\text{Ga}_5\text{As}_5\text{S}_{65}$	2.58	0.6 - 7	850

* <http://www.amorphousmaterials.com/Amtir-1.htm>

The next important step was infiltration of this long period opal structure with chalcogenide glass. Table I indicates the physical properties of some arsenic and selenium

containing compounds. We used the commercial blend called AMTIR-1. Pressure assisted the infiltration process at 600°C.

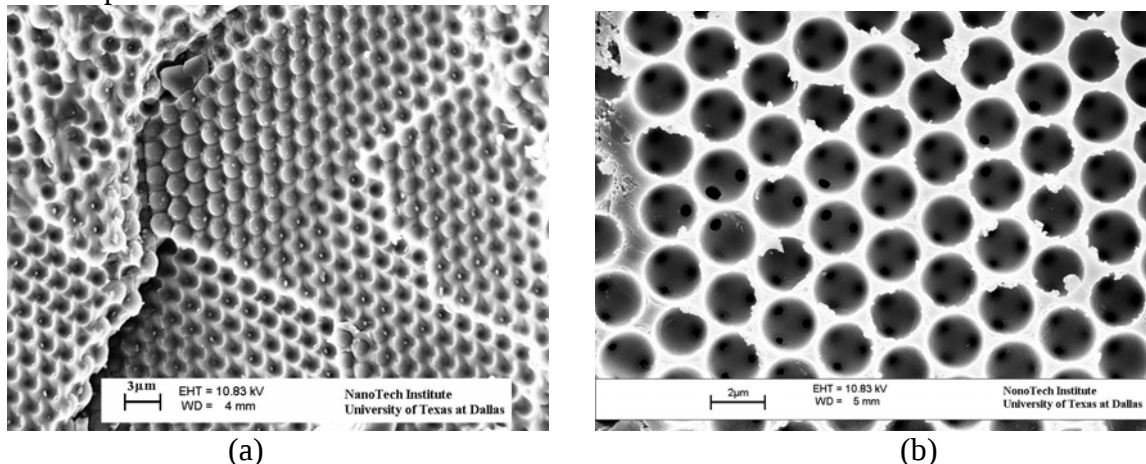


Figure 9: Left: SEM image of the cleaved edge of the chalcogenide glass-silica opal composite with ~100% infiltration. Right: image of the chalcogenide glass inverse opal with the silica glass dissolved away. The channels between voids are easily seen. The original particle diameter of the template was 2.3μm. After sintering the distance between particles reduced to 2μm

The final step in using these materials would be to break up the beautiful inverse opal structure of Figure 9(b) into a coarse powder that would have substantial infrared reflectivity. This powder would be the “white” infrared pigment that we refer to. It would be entirely analogous to a coarse polycrystalline mass of TiO_2 particles, that looks brilliant white in the visible regime. We have measured reflectivity up to 60%-70%, but that has to be merely a lower limit since it was difficult to collect all the scattered optical radiation. An integrating sphere measurement would have been most decisive as to the degree of infrared “whiteness” that would be observed.

The fabrication outlined above is ready to be adapted for the creation of a useful pigment that consists of a porous mass of inverse opal material. For further conclusions on this project, please see the Executive Summary at the beginning.

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(1) List of Publications

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"In-situ spectroscopic investigations of electrochromic cells that use dioxithiophene-based conjugated polymers," J Hwang, M Nikolou, B Ihas, R Clark, M Cornick, DB Tanner, I Schwendeman, and JR Reynolds.

"Line patterning for flexible and laterally configured electrochromic devices," AA Argun, and JR Reynolds.

“Modulation and Switching Kinetics at 8-12 um based on the electrochromism of Poly(3,4-ethylenedioxythiophene),” I Jin, and B Dunn.

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Hieu Duong - Ph.D. 9/16/03

Il-Sup Jin, Ph.D.

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Gregory Mitchell Ph.D., 3/21/03

Yuko Miyahara, M.S. 2002

Kwang-Fu Shen - Ph.D., 3/25/04

Derald Tucker - M.S. 2003

Qichun Zhang - M.A., 3/25/04

University of Florida:

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Eli Yablonovitch received the 2001 Julius Springer Award.

Eli Yablonovitch was elected to the National Academies of Sciences and National Academies of Engineering in 2003.

Fred Wudl, Member, American Academy of Arts and Sciences

Fred Wudl received the Herbert Newby McCoy Award

Bruce Dunn appointed to Editorial Board of *Solid State Ionics*

Irina Schwendeman received the Butler Polymer Research Award 2001 and the Outstanding Academic Achievement Award, UF International Student Office, 2001

(3) Report of inventions

JR Reynolds, K Zong I Schwendeman, G Sonmez, P Schottland, A Argun; PH Aubert, "Electrochromic Polymers and Polymer Electrochromic Devices," U.S. Patent No. 6,791,738 B2 issued Sept 14, 2004.

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(4) Technology Transfer

SRI International, Palo Alto