

Titanium Dioxide based Electrochromic Iris

Preparation, Characterization and Application

C. Kortz, A. Hein and E. Oesterschulze

*Physics and Technology of Nanostructures, University of Kaiserslautern, Erwin-Schroedinger-Strasse 46,
67663 Kaiserslautern, Germany*

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Abstract: The miniaturization of a classical iris consisting of blades which are moved towards the path of light is limited, due to the size of the actuators and the additional space needed for blade storage when the iris is completely open. To overcome these limitations we present a fast switching, non-mechanical micro iris based on electrochromic molecules, namely viologens, which are adsorbed onto a titanium dioxide nanoporous electrode. Measurements of the energy consumption, the response time and the spectral light transmission are presented. The complete fabrication route and the life time of the device are discussed in detail.

1 INTRODUCTION

The realization of a miniaturized iris comes to interest since more and more commercially available hand-held electronics were equipped with integrated cameras. Due to the small size of these cameras a classical blade iris cannot be integrated. An active iris is indispensable for both the intensity and in particular the depth of focus control.

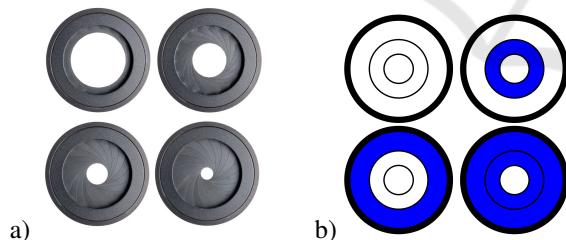


Figure 1: a) Images of a classical iris. In the upper left corner the iris is completely open and only the blade storage is left to be seen. This extra space is too big for micro iris applications for integrated camera systems. b) A schematic view of an electrochromic iris: the device can be switched completely transparent, only a small area around the iris is needed for sealing. This device can be miniaturized to fit the conditions in integrated optics.

The major reason why there is no iris integrated in small cameras is the required space. Especially when the iris is completely open the blades have to be moved outside the path of light and have to be stored in an additional ring shaped space (see Fig. 1a)), which is not available in micro optical devices.

Different solutions were presented to build up

miniaturised iris devices based on microelectromechanical systems (MEMS), liquid displacement techniques and electrochromic devices (Syms et al., 2004) (Kimmle et al., 2011) (Deutschmann et al., 2015).

MEMS based iris devices have a similar working principle as a classical blade iris (Yu et al., 2012). A shutter is moved towards the path of light to realize the iris function. The advantage of MEMS based devices is the fast switching time. They can be miniaturized easily but the dimensions of the device are much larger than the path of light and high voltages of more than 80 V are needed to move the blades. So they do not fit the conditions for integrated optics in battery powered hand-held electronics.

Another approach is to move light absorbing liquids, like oil or ink into the path of light to create an iris (Kimmle et al., 2011). The advantage is that in this case the storage does not have to be ring shaped around the optical path, but can be designed freely. Nevertheless an additional space and actuators have to be provided (Müller et al., 2012).

2 STATE OF THE ART

One approach to create a non-mechanical iris was using electrochromic molecules which change their absorption by applying a chemical potential (Roth et al., 2011). Multiple designs and molecules were tested (Deutschmann and Oesterschulze, 2014). The latest iris was based on two complementary electrochromic molecules, which were dissolved in the electrolyte encapsulated between two transparent conducting ox-

ide (TCO) coated glass sheets used as electrodes (Deutschmann et al., 2015). If a voltage is applied between these two electrodes the liquid turned from transparent to almost black. This coloring process is reversible, without any need for storage space. To create the iris, the TCO layers were structured by UV lithography. The dissolved electrochromophores were only colored if the potential was applied at the desired rings which form the iris shape (see Fig. 1b)). A diffusional blurring of the iris structure was observed which slightly influenced the iris function (Pätz et al., 2014).

The optical properties and the space and power requirements of this non-mechanical iris were satisfactory for integrated optics. But this design suffered from long response times. Especially, the bleaching took at least 20 s and longer. However, for consumer electronics response times in a sub-second range are required.

3 EXPERIMENTAL PROCEDURE

A transparent electrochromic iris device is realized using two TCO coated glass substrates. These glasses were cleaned in an ultrasonic bath using acetone, isopropanol and DI water for 5 min each and dried under nitrogen flux. Alignment marks and contact pads made of 10 nm Cr and 90 nm Au were added to the TCO layer using magnetron sputtering and lift-off-technique. In the next step, a paste containing titanium dioxide (TiO_2) nanoparticles with a diameter of 10-15 nm (Solaronix Ti-Nanoxide T/SP) was applied by doctor-blading technique. To get the final porous structure, the samples had to be heated up to 450°C on a hot plate and subsequently to 550°C with a ramp of $10^\circ\text{C}/\text{min}$ in a vacuum furnace. This temperature was held for 2 h and the samples were cooled naturally. The shape of the iris was created by laser structuring. With this procedure the TiO_2 and the TCO layers were structured in the same step. After this preparation of the working electrode it was immersed in a solution containing the viologen and kept there for several hours.

The viologen we used in our experiments had a phosphonate anchor group to ensure a surface occupancy on the TiO_2 nanoporous layer, as seen in Fig. 2. After the fictionalization was completed, the samples were rinsed in ethanol and dried under nitrogen flux. To build up a working device a second TCO coated glass was bonded to the working electrode using a UV-structurable spacer (Ordyl, Elga Europe). The later carrying the cavity for the electrolyte. This cavity could be filled and sealed hermetically to prevent

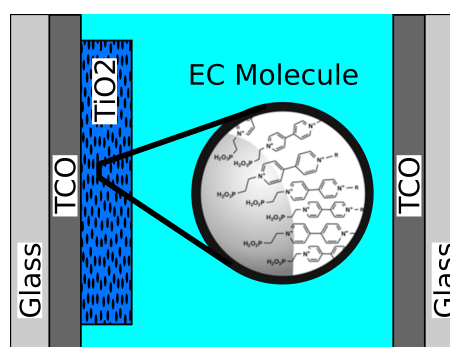


Figure 2: Schematic illustration of the electrochemical cell device: the working electrode with nanoporous TiO_2 and attached viologen on the left and the counter electrode on the right side. The electrolyte in between provides charge exchange among the electrodes.

oxygen and moisture infiltration.

Our goal is to realize an iris that fits all restrictions of miniaturized integrated camera systems for consumer applications, which are:

- low space requirements;
- low power consumption;
- fast switching;
- high contrast;
- long lifetime.

These challenging restrictions are the major reasons why integrated cameras are not equipped with an iris yet.

4 RESULTS AND DISCUSSION

Each of the following sections addresses one of the mentioned challenges. The newly developed solutions, achievements and the current state of the research are discussed in detail.

4.1 Structuring

The structuring of TiO_2 based electrochromic devices is challenging, because the preferred UV lithography techniques fail due to side reactions between the photoresist and the TiO_2 nanoparticles during exposure. For our device we chose to transfer the iris structure into the nanoparticle layer by laser ablation (Roth, 2013).

With this method, the nanoparticle layer and the TCO layer were structured simultaneously. As seen in Fig. 3 the different iris rings are separated clearly

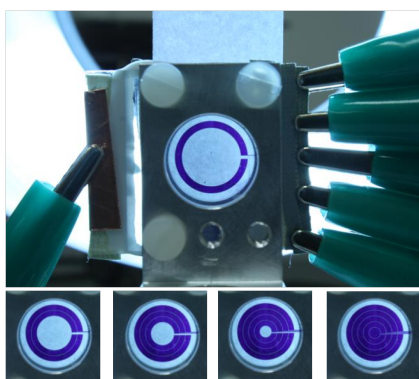


Figure 3: Images of a TiO_2 based iris in different switching states (Roth, 2013).

from each other revealing a sharp edge. The conductor track to the contact pads on the right side interrupts the outer rings.

4.2 Electrical Requirements

The electrical response was investigated operating the working electrode in a cuvette using a commercially available Ag/AgCl reference electrode and a Pt wire as counter electrode. The electrolyte consisted of $1 \frac{\text{mol}}{\text{l}}$ LiClO_4 salt solved in propylene carbonate. To secure that no oxygen affects the measurement, the electrolyte was bubbled for at least 15 min with nitrogen before use. The electric potential was applied and the current was measured by a potentiostat (Reference600, Gamry Instruments). The potential between the working electrode and the electrolyte leads to a change in the redox state of the viologen. When a negative potential is applied, the viologen molecules are reduced and they change their color from transparent to absorbing, resulting in a negative current. Reversing the potential leads to the oxidation of the viologen and they turn transparent again, resulting in a positive current. This process is fast and reversible. To keep the redox state no further current is needed; a phenomenon that is called memory effect.

One of the restrictions for miniaturized iris devices is low power consumption. As seen in Fig. 4 the maximum current needed to change the color of the device was approximately 0.8 mA at a potential of 0.55 V. This leads to a total maximum power of 0.44 mW, which can easily be provided by battery power. As can be seen in Fig. 4 the current drops rapidly after reaching its maximum value.

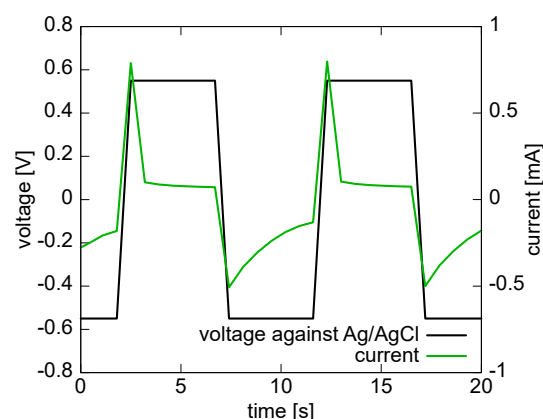


Figure 4: Electrical response of the electrochromic working electrode. A step potential was applied against a Ag/AgCl reference electrode and the current was measured.

4.3 Electro-Chromophoric Response

The electro-chromophoric response was also measured in the previously described setup using a Ag/AgCl reference electrode and a Pt counter electrode in the same electrolyte. To observe the coloration, a homogeneous filter with an unstructured working electrode was investigated. This filter was illuminated by a white light source (KL 1500 LCD, Schott) and the transmitted light was analyzed using an integrating sphere and a spectrometer (Flame, Ocean Optics). To characterize the performance of our device, the transmitted intensity was integrated from 450 nm to 750 nm and recorded time-resolved.

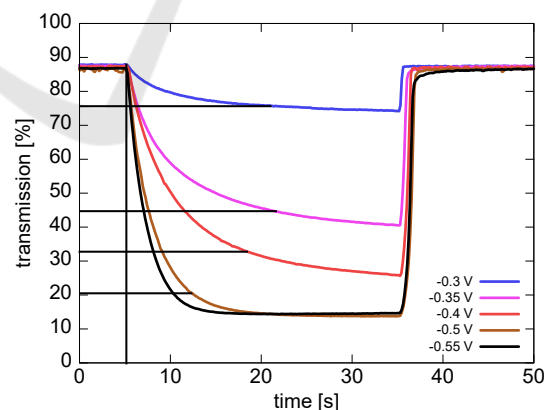


Figure 5: Time-resolved transmission through a homogeneous electro-chromic filter operated at different potentials.

Figure 5 shows the integrated intensity, where 100% stands for the light transmitted through the measurement setup without the working electrode. The maximum transmission through the working electrode was 88% in the transparent state. The minimum transmission T_{\min} was 14% in the opaque state

Table 1: Results taken from Fig. 5: minimum transmission and response time at different applied potentials.

U [V]	T_{\min} [%]	t_c [s]	t_b [s]
-0.3	73.8	16.0	0.2
-0.35	40.5	15.7	0.8
-0.4	25.5	13.4	1.2
-0.5	13.3	7.2	1.6
-0.55	13.7	5.2	1.5

at a potential of -0.55 V.

The response time was defined as the time where 90% of the equilibrium transmission is reached, indicated by the horizontal lines in Fig. 5. We observed a response time for coloration of $t_c = 5.0$ s and for bleaching of $t_b = 1.5$ s when applying a potential of ± 0.55 V.

The equilibrium transmission in the opaque state can be controlled by the thickness of the TiO_2 layer, the species and amount of EC-molecules adsorbed onto the TiO_2 surface and the applied voltage. The different T_{\min} responding to different applied potentials are shown in Fig. 5, too. It is obvious that the time for coloration is larger for low potentials although the change in transmission is also low. The resulting t_b values do not strongly vary. The results are summarized in Tab. 1.

The main reason why we do not reach 0% in the colored state is the spectral characteristic of the used viologen molecule. As can be seen in Fig. 6 the absorption deviates from the neutral behavior at the wavelengths range from 450 nm to 750 nm. Especially around 500 nm and 750 nm large transmission in the colored state can be observed which is characteristic for viologen molecules. This can affect the function of the iris, especially the depth of focus control, which was discussed in detail in (Pätz et al., 2014). The depth of focus differs compared to a classical iris depending on the transmission through the opaque region. Thus an effective aperture diameter has to be defined to achieve comparable depth of focus results.

In the transparent state we see a high transmission which is constant over a large spectral range but drops at 500 nm and shorter wavelengths. This behavior can be explained by the absorption of the TCO, TiO_2 and the viologen in its transparent state.

4.4 Hermetic Sealing

The device consists of two TCO coated glass sheets with the mesoporous structure carrying the viologen and the electrolyte in between. It was critical for the electrolyte to be sealed leak proof and bubble free in

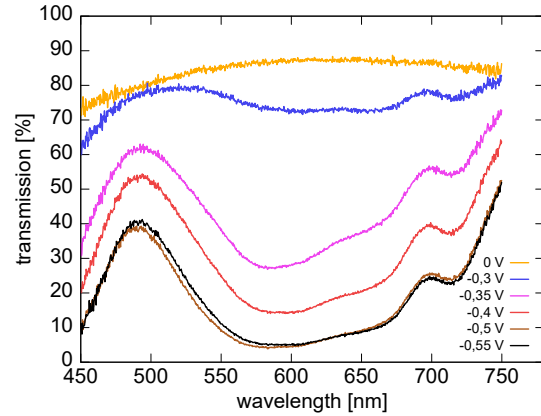


Figure 6: Spectral transmission through a homogeneous viologen functionalized TiO_2 layer on a TCO substrate at different potentials.

the cavity between the glass sheets. But not only the loss of the electrolyte destroys the function of the device, the penetration of oxygen and water affects the switching, too. So even without a leakage, the functionality of the device was reduced after days when a non-hermetic sealant was used. So we included an oxygen proof sealing made of UV curing adhesive. This raised the durability of our cell from days to months in first tests. Further investigations have to be made in this field of interest to realize a durable electrochromic device with the smallest possible dimensions.

5 CONCLUSION

A new approach to realize a non-mechanical miniaturized iris based on viologen adsorbed onto nanoporous TiO_2 was presented. The laser structuring of the nanoporous TiO_2 layer showed satisfactory results and the power consumption of the electrochromic layer was suitable for battery powered devices. The minimum transmission in the colored state reached 14% and could be varied by the applied potentials which led to different response times of the electrochromic layer. For long live stability a hermetical sealing was used to ensure an oxygen and moisture free electrolyte. This was realized by UV curing adhesives.

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