Mesoporous Materials

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A High-Speed Passive-Matrix Electrochromic Display Using a Mesoporous TiO_2 Electrode with Vertical Porosity

Wu Weng, Tetsuya Higuchi, Masao Suzuki, Toshimi Fukuoka, Takeshi Shimomura, Masatoshi Ono, Logudurai Radhakrishnan, Hongjing Wang, Norihiro Suzuki, Hamid Oveisi, and Yusuke Yamauchi**

Recently, the application of electronic paper (E-paper) has attracted considerable attention. Many types of reflective displays, such as reflective liquid crystal displays[1] and electrophoretic displays,[2,3] have been introduced and applied to E-paper. Among them, electrochromic materials, which change in color intensity when an appropriate potential is applied, are the subject of an increasing number of reports.[4–6] Recently, polymers such as poly(3,4-ethylenedioxythiophene) (PEDOT) or catenanes were reported to show electrochromic behavior.[7–9] The slow response time for coloring has been a serious problem with these kinds of polymers. As probable electrochromic materials, viologens have commonly been utilized for electrochromic displays (ECDs). Many studies have focused on viologen-modified microspheres or nanostructures to increase the switching speed.[10–16] Viologens are basically blue in color, and it is thus difficult to realize a full-color display. Furthermore, these kinds of displays have a common drawback: poor background whiteness.

To date, electronic displays have not been able to meet the requirements necessary for extensive practical applications. Currently, full-color reflective displays that demonstrate a fast response time are in much demand. Usually, display devices are driven by either active-matrix drive mode or passive-matrix drive mode. Active-matrix drive mode is very fast, but it needs expensive thin-film transistors (TFT) for all the pixels of the display, which leads to a high price. Passive-matrix drive mode does not need such expensive electric elements, and it has a simple, low-cost structure. However, when ECD devices are driven by passive-matrix mode at high scanning speed, the drift of electrochromic materials around the electrode leads to poor resolution. That is, the display images are blurry.

Herein, we aim to realize high scanning speed and high display quality. We focused on leuco dyes, which are well known as recording materials in thermal imaging systems, because the leuco dyes show a wide variety of colors and are commercially available.[17,18] We demonstrated a high-speed and high-resolution electrochromic passive-matrix display using a leuco dye with a mesoporous TiO_2 electrode with vertical pores (Figure 1). The vertical pores of the electrode can support effective diffusion of leuco dyes perpendicular to the electrode and can prevent the diffusion of the dye around the electrode. Since the colorless state of this kind of display is transparent, it exhibits better background whiteness, which improves readability and reduces eyestrain.[19,20] Furthermore, the application of leuco dyes to ECD devices has high potential to realize a full-color reflective display with low production costs. These features are very desirable for future E-paper applications.

Our device, which consists of two electrodes (working electrode and counter electrode) and electrolyte (Figure 1), was driven by the passive-matrix driving method (an addressing scheme used in earlier liquid crystal displays).[21,22] Each electrode has striped indium–tin-oxide (ITO) layers 420 μm wide on a glass substrate (Figure 1b and Figure S1 in the Supporting Information). The mesoporous TiO_2 film was grown only on the observation side of the working electrode. By improving the previous method,[23] continuous TiO_2 films with highly ordered mesostructure and vertical pores were uniformly prepared on the working electrodes by spin coating with a precursor solution. The film thicknesses were changed by using different spinning speeds. Thicknesses of approximately 300, 200, and 100 nm were realized by speeds of 2000, 4000, and 6000 rpm, respectively. Cross-sectional and top-surface SEM images showed that mesopores were oriented vertically with respect to the substrate (Figure S1c in the Supporting Information). The mesochannel walls are composed of periodically arranged cages with connecting necks between the neighboring cages (see the Supporting Information, in particular Figure S2, for details). The two electrodes sandwiched the electrolyte so that the striped ITO layers were orthogonally crossed (Figure 1b and Figure S3 in the Supporting Information). The electrolytic solution consisted of black leuco dye (2-(3′-trifluoromethylphenylamino)-6′-

[*] W. Weng, T. Higuchi, M. Suzuki, T. Fukuoka, Dr. T. Shimomura, Dr. M. Ono
Funai Electric Advanced Applied Technology Research Institute Inc.
2-1-6 Sengen, Tsukuba, Ibaraki 305-0047 (Japan)
E-mail: weng.w@funai-atri.co.jp
Dr. L. Radhakrishnan, H. Wang, Dr. N. Suzuki, H. Oveisi, Prof. Dr. Y. Yamauchi
World Premier International (WPI) Research Center for Materials Nanoarchitectonics (MANA)
National Institute for Materials Science (NIMS)
1-1 Namiki, Tsukuba, Ibaraki 305-0044 (Japan)
E-mail: yamauchi.yusuke@nims.go.jp
Homepage: http://www.nims.go.jp/mana/members/independent_scientist/y_yamauchi/index.html
Prof. Dr. Y. Yamauchi
PRESTO (Japan) Science and Technology Agency (JST)
5 Sanban-cho, Chiyoda, Tokyo 102-0075 (Japan)

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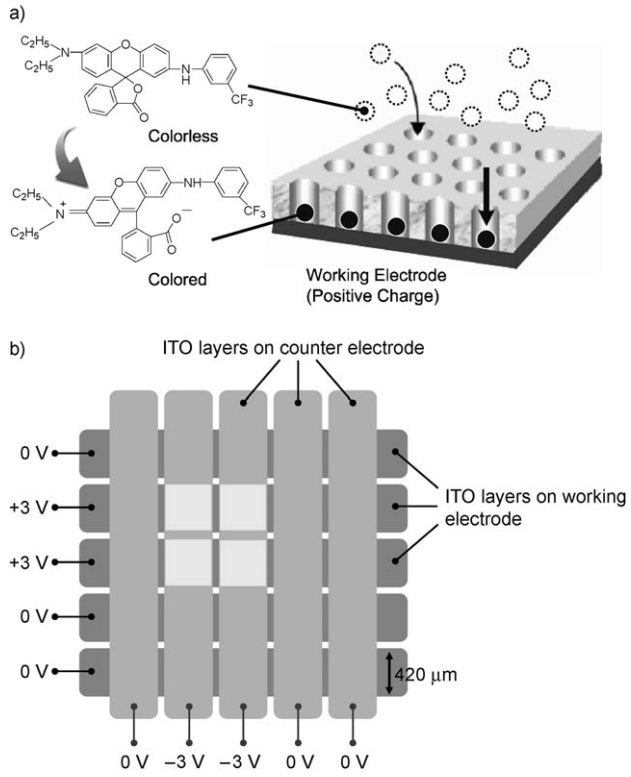

Figure 1. a) Mechanism of imaging using a leuco dye on a mesoporous TiO_2 electrode with vertical pores. Imaging and erasing are carried out by applying a potential of ± 3.0 V to the device. The leuco dye is changed to its colored form on the surface of the working electrode when an electric current is applied. The colored dye changes back to the colorless form when a reverse electric current is applied to the electrodes. b) Imaging process for a passive-matrix electrochromic display. The working electrode (with mesoporous structure) and counter electrode (without mesoporous structure) are arranged orthogonally. The points of intersection of the electrodes are colorable positions. The electrode has striped ITO layers 420 μm wide and separated by 30 μm on a glass substrate.

(diethylamino)fluoran), electron acceptors (dibenzyl), and electron donors (dimethylhydroquinone) dissolved in organic solvent (dimethylacetamide).[20]

Imaging and erasing can be carried out by applying a potential of ± 3.0 V to the device. When electric current is applied between two electrodes, the colorless leuco dye changes to its colored form (i.e., imaging) by donating electrons to the surface of the positive electrode. When reverse electric current is applied, the dye changes back to the colorless form (i.e., erasing). The changes in leuco dye structures (oxidation and reduction behavior) are shown in Figure 1. The crossed sections of striped ITO layers are the pixels of the matrix, which can be passively driven individually and independently (Figure 1b). The UV/Vis absorption spectrum of the colored display showed two peaks in the visible regions centered at 450 and 600 nm, while no apparent peaks were observed in the spectrum of the bleached display (Figure S4 in the Supporting Information).

Figure 2 shows the display images of checkered patterns at various driving speeds. Although display images normally blur with increasing scan speed, we achieved fast driving

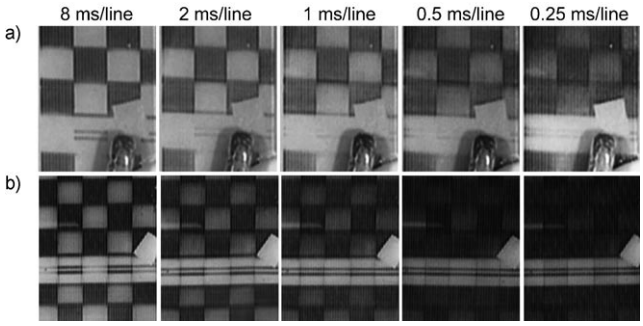

Figure 2. Comparison of display images with checkered patterns (8 mm × 8 mm). a) Mesoporous TiO_2 electrode (200 nm thick) prepared by spin coating at 4000 rpm. b) TiO_2 electrode without mesoporous layers.

speeds with high contrast ratios by utilizing mesoporous TiO_2 electrodes (Figure 2a). In the case of an electrode without mesoporous TiO_2 film coating (Figure 2b), the image blurred even at a low scan speed of 2 ms per line owing to the drifting of colored leuco dye molecules. The reflectance of colorless regions in checkered patterns of mesoporous TiO_2 electrode showed values twice as high as that of unmodified electrodes (Figure 3). Thus, the vertical mesoporous structure prevented the drifting of colored leuco dye molecules. This effect keeps

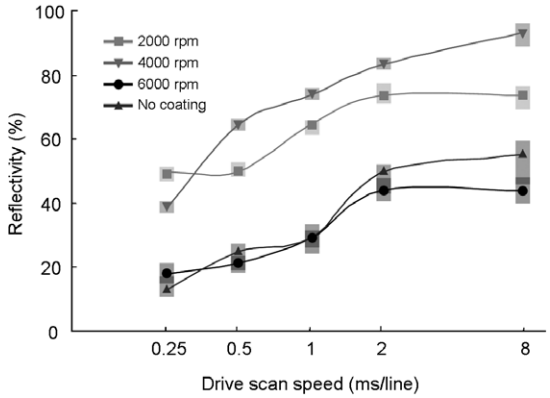

Figure 3. Reflectivity dependence on driving speed. Each data point indicates the average of the reflectivity in the colorless positions of the checkered patterns of Figure 2. Over 100 colorless positions were measured to calculate the average values.

pixels without current in the white state and makes the image clear. The white-state reflectance was improved significantly. Upon writing, the clear images remain on our display for a few minutes without becoming blurry.

The highest white-state reflectance of the mesoporous TiO_2 electrode at a scan speed of 8 ms per line was over 90%. To our knowledge, this is one of the best reported results for an ECD. Currently, almost all existing ECDs are used as window glass[24] or as rearview mirrors for cars[25] rather than in display applications. Although some electrochromic materials, such as viologens, have been used in display devices, all of these devices were segment-type displays (i.e., characters and images on the screen were fixed.). Therefore, it is nonsense to compare them to our system. Our system can

display various characters and images on the same screen and can act as E-paper. The white-state reflectance achieved herein is far higher than that of existing E-paper, such as the E-ink or Bridgestone devices, both of which were reported to have values below 45%.

The reusability of the electrolyte was tested by applying a triangular wave pattern (±3.0 V) to a 1.0 cm^2 cell (1 cm × 1 cm) consisting of two ITO electrodes and electrolyte sandwiched between them. This method is a well-known endurance test for electrochromic materials.[20] This cell is equivalent to one pixel of our display. The experimental result showed clear images with no degradation of image density and background density even after over 1000000 cycle operations (imaging and erasing).

We also found that the thickness of the mesoporous layer critically affects the contrast of the displayed image. Thinner mesoporous layers led to poorer contrast. The electrode with a mesoporous TiO_2 layer 100 nm thick exhibited almost the same results as the electrode without the mesoporous layer. Leuco dyes came into the vertical pores, colored on the surface of the ITO layer, and then quickly left the thin pores owing to the short length of the mesochannels. Therefore, image blurring occurred even at a low scan speed of 2 ms per line. On the other hand, the thickest TiO_2 film showed lower reflectance (Figure 3 and Figure S5b in the Supporting Information). The thickest film prevented fast diffusion of leuco dyes in the vertical direction. Furthermore, the drifting of colored leuco dye molecules occurred through the windows among the vertical pores. We obtained the best results from mesoporous TiO_2 of 200 nm thickness. We can expect to get a clearer display image at faster driving speeds by optimizing the pore diameter and the lengths of the mesoporous channels.

In summary, we have successfully realized a high-speed and high-quality passive-matrix ECD using leuco dyes by applying a TiO_2 nanoporous array on the electrode. It will be possible to have higher a contrast ratio at faster scan speed by applying mesoporous TiO_2 array on the electrode. The vertical pores of the mesoporous films effectively prevented the drifting of the leuco dye molecules. We thus demonstrate that ECD devices can be operated at an ultrafast driving speed (less than 1 ms per line), which is faster than that of existing electronic paper. Our ECD is a promising candidate for future reflective display devices. Moreover, we realized multicolor displays by using various leuco dyes. The display image of a prototype of a 5.0 cm × 5.0 cm ECD device is shown in Figure S6 in the Supporting Information. We believe that this work will open new avenues to full-colored passive-matrix electrochromic displays.

Experimental Section

Preparation of mesoporous TiO_2 films with vertical pores: The precursor solution was prepared according to the previous procedure.[23] The ethanol-based precursor solution including $TiCl_4$ and F127 was spin coated on substrates at room temperature. Before use, the substrates were washed carefully with acetone and water, which is very important to achieve high reproducibility. The spin-coating method was selected because it yields highly uniform films and allows the thickness of the films to be controlled. The spinning speed and time were fixed at 2000, 4000, 6000 rpm and 30 sec to form thin films with different thicknesses. Thickness of approximately 300, 200, and 100 nm were realized at speeds of 2000, 4000, and 6000 rpm, respectively. As-prepared thin films were aged under low-humidity and low-temperature conditions (−20 °C and 20% relative humidity (RH)) for 72 h.[26] After aging, all films were calcined at 350 °C for 4 h.

Device fabrication: Our passive-matrix electrochromic display consisted of two electrodes. The working electrode (with mesoporous structure) and counter electrode (without mesoporous structure) are orthogonally crossed. A plastic substrate was used as spacer to make a uniform gap (60 μm) between the working and counter electrodes. The electrolyte solution including about 7.15 wt% (0.2 mol L^{-1}) leuco dye was sandwiched between the two electrodes. The electrode cell was held with commercially available tweezers. The electrode has striped ITO layers 420 μm wide and separated by 30 μm intervals on a glass substrate. As is seen in Figure 1b, the points of intersection of the electrodes are colorable positions. Imaging and erasing are carried out by applying a potential of ±3.0 V to the device.

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