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## Enhanced Electrochromism in Gyroid-Structured Vanadium Pentoxide

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The reversible, persistent electrochromic change in color or transparency controlled by a temporarily applied electrical potential is attractive because of its low energy consumption.<sup>[1,2]</sup> While electrochromic materials have been employed in smart windows and display devices, only very few electrochromic products are commercially available,<sup>[3]</sup> despite extensive research for over 40 years.<sup>[4]</sup> This is mainly due to long switching times, low chromatic contrasts, and unsatisfying coloration efficiencies.<sup>[5]</sup> Our study demonstrates that vanadium pentoxide patterned in a three-dimensional highly interconnected periodic nanomorphology substantially enhances the electrochromic performance, with switching speeds approaching video rate. Our nanofabrication strategy employs electroplating of vanadium pentoxide into a mesoporous polymer template that was obtained by self-assembly into a double-gyroid (DG) morphology. This patterning technique can be applied to most electroplatable inorganic and polymeric materials for use in enhanced electrochromic devices.

Following Deb's discovery of tungsten oxide electrochromism in 1969, numerous other transition-metal oxides, such as vanadium pentoxide, were found to be electrochromic.<sup>[4,6]</sup> Because of their simple multilayer design, largesurface-area electrochromic devices can be cheaply manufactured.<sup>[2]</sup> Typically, the conducting metal oxide film forms the chromogenic electrode, which is separated from the chargebalancing counter electrode by an electrolyte (**Figure 1**f). The reversible optical absorption change is caused by an electrontransfer reaction accompanied by a compensating transfer of mobile cations (I<sup>+</sup>) between the metal oxide (MO) and electrolyte;<sup>[5]</sup>

$$MO + xe^{-} + xI^{+} \rightleftharpoons I_{x}MO$$

This double injection of ions and electrons maintains electroneutrality of the system. An operating potential of only a few volts is sufficient to control the direction and magnitude of the transferred charge and the resulting optical properties.

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Moreover, little or no input of power is needed to maintain a specific redox state, which leads to the desired optical memory effect.<sup>[1]</sup> As a low-cost, low-power, and low-voltage technology, it is highly attractive for a wide range of potential applications.

Conventional flat film devices suffer, however, from limited ion intercalation and therefore from a poor electrochromic performance. The chromatic contrast  $\Delta T(\lambda)$  between the colored and bleached state is limited by finite ion penetration depths, while the switching time  $\tau$  is restricted by the long diffusion distances required to achieve a satisfactory color saturation.<sup>[7]</sup> A simple solution to this problem is the formation of a network structure.<sup>[8]</sup> The formation of a nanostructure in the intercalation compound not only enables the expansion and contraction of the host material during guest insertion and extraction, but also increases the surface-to-volume ratio. In particular, an increase of the specific surface area is generally expected to significantly reduce the characteristic diffusion length of intercalation ions, while simultaneously increasing the number of accessible intercalation sites.<sup>[9]</sup>

Vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) is an abundant, low-cost material that is commonly used in electrochromic cells<sup>[10]</sup> and other intercalation applications such as high-energy-density batteries,<sup>[11]</sup> supercapacitors,<sup>[12]</sup> and sensors.<sup>[13]</sup> Recently, V<sub>2</sub>O<sub>5</sub> synthesis has focused on the manufacture of nanostructured or mesoporous scaffolds with the aim to improve its lithium ion intercalation properties, which are limited by an inherently low diffusion coefficient ( $D \le 10^{-12}$  cm<sup>2</sup> s<sup>-1</sup>) and a moderate electrical conductivity ( $10^{-2}$  S cm<sup>-1</sup>  $\le \sigma \le 10^{-3}$  S cm<sup>-1</sup>).<sup>[9]</sup> Nanomaterials of undoped vanadia employed in electrochromic studies include nanowires,<sup>[14–16]</sup> inverse opals (IOs),<sup>[8]</sup> and mesoporous films.<sup>[17]</sup>

Although these recent attempts brought about an improvement in electrochromic performance, the reported switching times remained 1-2 orders of magnitude above the desired video rate of 24 frames per second.<sup>[8,14-17]</sup> This is mainly due to the use of sub-optimal V2O5 morphologies in terms of their structural dimension, connectivity, and integrity. Conceptually, an ideal chromogenic material should be a mesoporous fully interconnected network consisting of struts with a homogeneous diameter and a narrow pore diameter distribution, enabling effective electrolyte infiltration and good charge transport. Small pore diameters (2-50 nm) give rise to dense highly porous films that can be made thin enough so that the assembled device has a low electrical resistivity. To enable response times below 100 ms the strut radius in the nanostructured device should be comparable to the lithium diffusion distance  $x = \sqrt{2Dt} \approx 5$  nm. Further reduction of the structural feature size is probably counterproductive because of the lowered conductivity, arising quantum effects, and lack of structural stability of the network.

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**Figure 1.** a-f) Schematic of gyroid self-assembly and vanadia replication. a) Surface modification with octyltrichlorosilane and SU-8 photoresist patterning. b) P(F)S-*b*-PLA film deposition and microphase separation of the block-copolymer into the DG morphology during annealing at 175 °C. The red styrenic majority matrix encloses the blue interconnected lactide network. The front face shows the characteristic double wave pattern of the (211) plane. c) Selective removal of lactide yields a mesoporous template. d) Electrodeposition of vanadium pentoxide in the voided network. The deposition process is restricted to areas that are not covered by SU-8, thereby creating a design pattern in the electroplated V<sub>2</sub>O<sub>5</sub>. e) Dissolution of the polymer matrix reveals the freestanding V<sub>2</sub>O<sub>5</sub> network. f) Assembly of a functional electrochromic nanodevice by capping with a transparent counter electrode and the injection of electrolyte. The application of  $\pm 1$  V induces a color change.

The DG morphology with  $Ia\overline{3}d$  symmetry arising from block-copolymer self-assembly is a promising candidate to fulfill the listed requirements.<sup>[18]</sup> A first successful application of a bicontinuous metal-oxide nanostructure based on the DG morphology has recently been demonstrated in dye-sensitized solar cells.<sup>[19]</sup> In contrast to this earlier example, a functional device based on the DG morphology that out-performs existing technologies has yet to be demonstrated.

Here, we report the replication of the voided DG blockcopolymer network into  $V_2O_5$  by electroplating, and its assembly into high-performance electrochromic devices. The procedure of our approach is illustrated in Figure 1.

The diblock copolymer used in this study is poly(4-fluorostyrene-r-styrene)-b-poly(D,L-lactide) (P(F)S-b-PLA) with a molecular weight of 23.8 kg mol<sup>-1</sup> and containing 39.9 wt% PLA, that is, 37.9 vol% PLA<sup>[20]</sup> (Figure 2f and Figure S2 in the Supporting Information). The styrene block with a 30 mol% content of fluorinated monomers was synthesized by atom transfer radical polymerization,<sup>[21]</sup> followed by the addition of lactide via organocatalytic ring-opening polymerization (see Supporting Information, Figure S1).<sup>[22]</sup> Importantly, both polymerization techniques offer precise and robust control over the copolymer composition, which is a requirement to reliably target the gyroid's narrow location in phase space.<sup>[18]</sup> Micrometer-thick polymer films were prepared on conductive fluorine-doped tin oxide (FTO) glass. Self-assembly of the two immiscible covalently bound polymer chains into the DG morphology occurs during brief annealing at 175  $^{\circ}\mathrm{C}$  for 20 min. Subsequently, the PLA minority phase was selectively removed by immersing the films in a mild alkaline solution. Figure 2a shows a scanning electron microscopy (SEM) image of such a voided bicontinuous DG film<sup>[23]</sup> with a volume fraction of approximately 62.1 vol% (Figure S3). A magnified view of the film free surface in Figure 2c shows the double wave pattern that is characteristic for the DG (211) plane, confirmed by the simulation in the inset. The cubic unit cell size of this simulation is ~41.5 ± 1 nm, with a corresponding pore diameter of 11.0 ± 0.3 nm and specific surface to bulk volume ratio of 161.4  $\mu$ m<sup>-1</sup> (Figures S7 and S8).

Full porosity extending across both film interfaces is a crucial requirement for the successful replication of the polymer scaffold by electroplating. This requires the prevention of preferential wetting of the substrate by P(F)S or PLA. This was achieved by cleaning the FTO surface in a piranha solution, followed by the deposition of a partial octyltrichlorosilane (OTS) monolayer, resulting in a water contact angle on the modified substrate of  $59^{\circ} \pm 5^{\circ}$ . The correct OTS coverage was the outcome of an optimization process. An insufficient coverage resulted in the release of film from the substrate during PLA etching, suggesting the presence of a PLA wetting layer that has formed at the substrate during film deposition and annealing. In contrast, a nonporous P(F)S wetting layer was found on substrates with high water contact angles. The FTO surface was further modified using standard photolithography to create an isolating SU-8 photoresist pattern, which locally inhibited electroplating. This yielded visible design patterns with electrochromic contrast.

Anodic deposition of  $V_2O_5$  into the polymer template<sup>[16,24]</sup> was performed at a constant potential of 1.5 V versus Ag/AgCl

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**Figure 2.** a–h) SEM images of the employed nanostructures, chemical structure, and photographs of the electrochromic device. a,b) Cross-sectional SEM images of mesoporous gyroid films on FTO substrates showing the styrenic template after selective removal of the minority PLA phase (a) and the electrochemically replicated vanadium pentoxide after template removal and annealing at 275°C for 2 h (b). c,d) The magnified free surfaces of the bicontinuous P(F)S template (c) and the V<sub>2</sub>O<sub>5</sub> replica (d) show the characteristic double wave pattern of the majority and minority DG phase, respectively. Simulations of the (211) plane with a unit cell dimension of 42 nm are displayed as insets. e) SEM image of a macroporous V<sub>2</sub>O<sub>5</sub> IO structure that was used as a reference. All SEM scale bars represent 200 nm. f) Chemical structure of P(F)S-*b*-PLA with P(F)S in red, PLA in blue, and the bifunctional initiator in black. g) Transparent electrochromic device consisting of a FTO/V<sub>2</sub>O<sub>5</sub>/LiClO<sub>4</sub>+PC/FTO layer sequence and a Ag/AgCl wire as reference electrode. h) The design pattern in the chromogenic DG film is the crest of the University of Cambridge (scale bar: 1 cm), showing the bluish gray reduced and the yellow-green oxidized state of the V<sub>2</sub>O<sub>5</sub> film (scale bar: 0.5 cm).

from a 1:1 mixture of deionized water and ethanol containing 1  $\mbox{M}$  VOSO<sub>4</sub>·*x*H<sub>2</sub>O (Figure S4). The low surface tension of ethanol enabled the infiltration of the hydrophobic P(F)S pores by the electrolyte. The gradual growth of vanadia that progressed from the FTO surface through the porous DG network was stopped after 120 s before reaching the free surface of the template to yield (1.1 ± 0.1) µm thick films as confirmed by SEM. Following V<sub>2</sub>O<sub>5</sub> deposition, the samples were heated to temperatures between 200 and 400 °C at a rate of 1 °C min<sup>-1</sup>. The highly periodic DG V<sub>2</sub>O<sub>5</sub> replica formed upon removal of the styrenic template by dissolution (Figures 2b,d) shows the preservation of the nanostructure throughout the film. This structural integrity persisted up to ≈300 °C, above which the formation of crystallites larger than the gyroid strut size destroyed the nanomorphology (Figure S5).

To investigate the role of the structure size, V<sub>2</sub>O<sub>5</sub> IOs using 400 nm polystyrene spheres as template were also prepared (Figure 2e).<sup>[8]</sup> Apart from the much larger structure size, the V<sub>2</sub>O<sub>5</sub> synthesis conditions were identical to the DG replication. The large IO pores led, however, to a much faster V<sub>2</sub>O<sub>5</sub> deposition rate compared to the DG mesopores, so that a deposition time of 30 s was sufficient to manufacture a (1.8 ± 0.2) µm thick layer compared to 120 s for the deposition of a similarly thick film into the DG matrix.

The assembly of the electrochromic cell was completed by capping with a FTO counter electrode using a precut thermoplastic gasket as spacer, infiltration with  $1 \text{ M LiClO}_4$  in propylene carbonate, insertion of a Ag/AgCl wire as reference electrode,

and finally sealing the device with epoxy glue to yield the device of Figure 2g.

The potential of the cells was cycled between -1 V and +1 V, giving rise to a color change from blue-gray to green-yellow as shown in Figure 2h. The electrochromic color change was quantified by time-resolved optical measurements. Figure 3a shows the spectral response of the DG in comparison with the IO (upper and lower panels, respectively). A cathodic potential of -1 V causes lithium intercalation into V<sub>2</sub>O<sub>5</sub>. In the DG-structured sample, this gives rise to a fairly homogeneous transmission of ca. 50% across the entire spectral range. Charge extraction under an anodic potential of +1 V causes very high transmission above 500 nm with substantial absorption in the 400-500 nm range, causing the yellow-green coloration. In comparison, the IO is less transparent over the entire spectral range, irrespective of the applied potential. While the color contrast of the DG benefits from a pronounced variation across the entire wavelength spectrum, the color change in the IO structure stems only from the 400-500 nm range. For visible wavelengths, the DG device shows a maximal transmission variation of  $\Delta T$  = 49.8% at  $\lambda$  = 430 nm, where the IO only reaches a value of  $\Delta T = 14.1\%$ .

A second important aspect of electrochromism is the temporal response under alternating potentials ( $\pm 1$  V). The DG showed sharp and distinct transitions between the colored/oxidized and bleached/reduced state (Figure 3b). This switching behavior was analyzed in more detail by monitoring the trans-



**Figure 3.** a–d) Comparison of the electrochromic performance of DG-nanopatterned  $V_2O_5$  devices (top row) with a macroporous IO structure (bottom row). a) Optical transmittance spectra of the colored (+1 V) and bleached (-1 V) states after application of the potential for 2 s. At  $\lambda = 430$  nm, a maximal coloration contrast of  $\Delta T = 49.8\%$  was measured for the gyroid device, in comparison to  $\Delta T = 14.1\%$  for the IO structure. b) Transmittance variation upon alternating 2 s potential steps (±1 V). The same color coding is used for the DG and IO devices. c) Switching curves extracted from (b) for  $\lambda = 430$  nm. The lines are fits of T (t) =  $T_0 + \Delta T e^{-t/\tau}$  to the data, where  $\tau$  is the characteristic switching time. d) Optical density  $|\Delta OD|$  at 430 nm versus the charge density | q | during ion intercalation (orange) and extraction (blue). Significantly higher changes in optical density were observed for the gyroid device compared to the IO for equal amounts of charge density passed through the cells.

mittance at 430 nm (Figure 3c). The characteristic response times were determined by fitting the exponential functions to the switching curves. The DG device showed short switching times of ( $82.5 \pm 2.9$ ) ms for the bleaching step and ( $86.7 \pm 2.3$ ) ms for the reverse process. In contrast, the IOs showed a much slower temporal response with switching times of 122 and 235 ms.

A further important requirement of electrochromic materials is cycle stability and stability of the structural integrity of the nanostructured material. Both investigated structures exhibited good long-term cycle stability with less than 20% drop in coloration contrast after hundreds of switching cycles. The V<sub>2</sub>O<sub>5</sub> nanostructure remained intact during extended cycling, as confirmed by SEM. The excellent electrochromic stability (over more than 100 cycles) has been demonstrated in a subsequent study.<sup>[25]</sup>

Finally, the charge per area q that was required to induce a steep gradient in optical density  $\Delta OD = \ln (T/T_0)$  was measured, where  $T_0$  is the initial transmittance (Figure 3d). The ratio of these two quantities defined the composite coloration efficiency  $CCE = \Delta OD/q$ . The ideal electrochromic material would display a large transmittance change with a small amount of charge, giving rise to a high CCE.<sup>[2,6,26]</sup> For the DG morphology, CCE values of -33.9 and -35.8 m<sup>2</sup> C<sup>-1</sup> for ion insertion and extraction respectively, were required to achieve a 95% switch at 430 nm. This corresponds to respective CCE values of -24.0 and -15.6 m<sup>2</sup> C<sup>-1</sup> of the IO V<sub>2</sub>O<sub>5</sub> morphology. These excellent CCE values are a direct consequence of the highly interconnected gyroid morphology, which combines a very high specific surface area, which provides good ion access, with a high electric conductivities.

In summary, we have demonstrated that manufacturing  $V_2O_5$  in a 3D periodic highly interconnected gyroid structure on the 10 nm length scale leads to a significant electrochromic performance enhancement. The structured devices surpass previous inorganic electrochromic materials in all relevant

parameters: the switching speed, coloration contrast, and composite coloration efficiency. Compared to planar or microstructured  $V_2O_5$ , devices with the 10 nm gyroid morphology combine a high coloration contrast with a high coloration efficiency. In particular, the 85 ms switching speed lies within a factor of two of video rate and is substantially faster than the switching rates of around 1 s that are typically reported for materials of this type. The enhanced ion intercalation into the DG morphology can be extended to other transition-metal oxides and is therefore promising for lithium ion batteries, supercapacitors, and sensors.

## **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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