bon source and carbonization was performed at 900 °C for 7 h [3,4]. The mesoporous carbon was then recovered by etching the silica in HF acid.

Characterization: Powder XRD analysis was performed using a Philips 1830 powder diffractometer with Cu Kα radiation (40 kV, 40 mA). Nitrogen sorption isotherms and textural properties of the materials were determined at −196 °C using nitrogen in a conventional volumetric technique by a Coulter SA3100 sorptometer. Before analysis the samples were oven dried at 150 °C and evacuated for 12 h at 200 °C under vacuum. The surface area was calculated using the BET method based on adsorption data in the partial pressure (P/P₀) range 0.05 to 0.2 and total pore volume was determined from the amount of the nitrogen adsorbed at P/P₀=0.99. Scanning electron microscopy (SEM) images were recorded using a JEOL JSM-820 scanning electron microscope. Samples were mounted using a conductive carbon double-sided sticky tape. A thin (ca. 10 nm) coating of gold sputter was deposited onto the samples to reduce the effects of charging. Transmission electron microscopy (TEM) images were recorded on a JEOL 2000-FX electron microscope operating at 200 kV. Samples for analysis were prepared by spreading them on a holey carbon film supported on a grid. Elemental analysis (of the nitrogen-doped carbons) was carried out using a CHNS analyzer (Fisons EA 1108). X-ray photoelectron spectroscopy (XPS) was performed using a Kratos AXIS ULTRA spectrometer with a mono-chromated Al Kα X-ray source (1486.6 eV) operated at 10 mA emission current and 15 kV anode potential. The analysis chamber pressure was better than 10⁻⁹ torr. FAT (fixed analyser transmission) mode was used, with pass energies of 160 eV (or 80 eV) for survey scans and 40 eV for high resolution scans. A magnetic immersion lens system allowed the area of analysis to be defined by apertures, a ‘slot’ aperture of 300 μm x 700 μm for wide/survey scans and a 110 μm aperture for high resolution scans. The take off angle for the photoelectron analyser was 90° and the acceptance angle was 30° (in magnetic lens modes). Data analysis was carried out using CASAXPS software with Kratos sensitivity factors to determine atomic % values from the peak areas. Charge correction was applied to the data at the processing stage.

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Switchable Electrochromic Images Based on a Combined Top–Down Bottom–Up Approach

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The recent development in mobile electronic equipment has boosted the demand for low-cost flat-panel displays. Today, 90% of the market is dominated by liquid-crystal displays (LCD), but new technologies such as organic light-emitting diode (OLED) and microencapsulated electrophoretic (MEP) displays have emerged recently.[1] Active or passive matrix addressable displays attract most commercial interest. However, for certain applications, other parameters, such as cost, power consumption, or high contrast are prevailing criteria, and switchable pictograms or icons are sufficient. The phenomenon of electrochromism is well known and involves electrically controlled light absorption in thin layers.[2,3] Alphanumeric electrochromic displays (ECDs) with structured working electrodes were described some time ago[4] and prototype active and passive matrix addressed systems have also been reported.[5,6] No reports on high-resolution electrochromic images (> 300 dots per inch (dpi)) are available. In mobile devices, power consumption is crucial. Icons that do not consume any energy except for switching between on and off are therefore advantageous. Recently, the role of electrochromics in this field has been recognized.[7] Switching in a millisecond or second range is possible, and essentially no energy is consumed to hold either state of information. Here we report on the preparation of electrochromic pictures of unprecedented resolution (360 dpi) and their incorporation in transparent and reflective ECDs. Our first version affords switchable high-resolution absorptive pictures between two optically


completely transparent glass plates. The technology is based on a combination of top–down (inkjet technology) and bottom–up ideas (molecular entrapping of electrochromophores in mesopores).

Viologens (N,N'-substituted 4,4'-bipyridinium salts) are well known electrochromophores exhibiting extinction coefficients from 1 to 4 × 10^4 in the reduced state.[9] The reversibility of the redox process and the stability in both oxidation states is demonstrated by the commercial success of viologens used in electrochromic auto-dimming rear-view mirrors.[5,10] An absorbance change of one, i.e., an easily readable optical transmission change of 90 %, is expected when approximately 400 monolayers on top of each other are switched, assuming a packing density per monolayer of 2.8 × 10^{-10} mol viologens cm^{-2} and Δλ = 1 × 10^4. This can be achieved using either viologen multilayer-modified optically transparent flat electrodes (OTEs) or a monolayer-modified transparent three-dimensional electrode with an inner surface area 400 times larger than its geometric area.

We recently reported on a remarkable amplification of coloration and improved switching times in electrochromic devices using a three-dimensional, mesoporous working electrode consisting of semiconducting sintered titanium dioxide nanocrystals modified with a self-assembled monolayer of 4,4'-bipyridinium salts.[11–15] The roughness factor (R), i.e., the accessible inner surface as compared with an ideally flat electrode, is 100 per micrometer of film thickness, resulting in an expected absorbance change of one for a film thickness of 4 μm according to Equation 1.

\[
ΔA = 10^3 I_{em} ε R
\]

where \(I_{em}\) is the surface concentration of the electrochromic moieties.[11]

For the preparation of homogeneously coloring working electrodes, the TiO2 film on FTO (fluorinated tin oxide) glass was, in previous work, exposed to a sub-millimolar solution of the relevant viologens modified with a TiO2-coordinating group such as a phosphonic acid functionality.[12] Under such conditions a complete coverage of all accessible coordination sites is observed within 10–20 min.

When reduced and kept at −0.6 V versus a silver/silver chloride reference electrode (Ag/AgCl), the affinity of the colored viologen towards the TiO2 drops considerably and some of the viologen is lost into the solution. This phenomenon did not represent a problem in electrochromic filter devices with a sandwich configuration of the working and counter electrode, since a minimum amount of solvent is used, forcing the dissolved viologen back to the TiO2-coordinating sites. However, in an electrochromic picture consisting of TiO2-anchored viologen pixels, such diffusion may result in continuous loss of the pictorial information by lateral diffusion of the viologen from occupied to unoccupied sites via the solution phase.

With this information in mind a procedure has been developed for the production of stable switchable electrochromic pictures. We decided to try inkjet printing as the deposition method, because several reports on the successful non-traditional application of inkjet printing in material science have appeared in recent years.[16–19]

The electrochromic picture was prepared using a personal computer (PC)[20] and a commercial inkjet compact disc (CD) printer. The caddy and the spacing of the printer were adapted to handle the TiO2/OTE/glass substrate and the ink orifices of the printer head were equipped with vessels for electrochromic ink instead of the original cartridges. The electrochromic ink consists of a viologen or a precursor thereof equipped with a phosphonic acid anchoring group and a further nucleophilic (1) or electrophilic (2) functional group (NAG, EAG in Fig. 1). The concentration of the ink is 0.1 M, resulting in 1.3 × 10^{-7} mol cm^{-2} of anchoring viologen, provided that the volume jetted for a 100 % colored area is

![Figure 1](http://example.com/fig1.png)

**Figure 1.** Cross-sectional of the electrochromic cell and zooming into the inkjet-printed crosslinked graphical information. a) Glass with OTE and 5 μm thick film TiO2 layer with inkjet-printed and crosslinked graphical information; b) mesoporous oxide layer partly covered with crosslinked electrochromophores; c) hypothetical structure of the crosslinked electrochromophores in a mesopore. 3a: trimethylene benzene.

1.3 μL cm^{-2}. The solvent and its ingredients are optimized for fine-droplet formation.[21] Adsorption of the phosphonated viologen from discrete droplets (ca. 16 pL) seems to proceed much faster than lateral spreading of the solvent resulting in electrochromic dots (Fig. 2d) with better quality than those observed with the original ink (magenta) on photo-quality inkjet printer paper (Fig. 2e).

The images received directly after inkjet printing were checked for their quality (absorbance, switching time, and stability). We found that the graphical information is originally excellent, but that the images are prone to smear or fade when they come into contact with protic polar solvents (e.g., aqueous ethanol). Moreover, after 4 months in a sealed cell in presence of γ-butyrolactone a distinct blooming was observed.[22] We have therefore developed the technique shown in Scheme 1 to fix the image via molecular crosslinking reactions. Moreover, this procedure results in a color amplification by introducing further viologen centers.
Depending on the nucleophilic or electrophilic nature of the inkjet printed viologen (1 or 2) the working electrode is treated with a solution of the counterpart electrophilic (EBB, 3 or 4) or nucleophilic (NBB, 5 or 6) building block. Notably, these are a multifunctional compounds without affinity to the TiO$_2$ surface, i.e., they will preferentially react at precursor/viologen-occupied sites. The procedure can be repeated using the sequence EBB–NBB–EBB–NBB and so on (Table 1). Finally, a treatment with a viologen containing a single electrophilic or nucleophilic end group (EEG or NEG, 7 or 8) is carried out in order to saturate all surviving reactive groups.

The effect of cascade reaction steps on the surface concentration $I'$ is shown in Table 1. In addition to this amplification, increased stability of the colored areas towards forced desorption is observed with the number of cascade cycles (Table 1, entries I–III).

In first samples an unwanted bluish tint in “white areas” related to a side reaction of the electrophilic building block compounds 3 and 4 with naked TiO$_2$ was observed. To suppress this side reaction, the electrode was treated with a solution of a repellent before each crosslinking step. Good repellents are long-chain alkyl phosphonic acids (11–13) or pyridinium ethyl phosphonic acid (10). The beneficial effect of such a treatment is documented in Table 1 (entries IV–IX).
A typical substructure obtained by the cascade reaction is shown in Figure 1c. Notably, the size of the structure can become larger than the diameter of the channels connecting the pores within the TiO₂ network. We have strong evidence that the stability of the pictorial information towards forced desorption is due to the mechanical entrapment of oligomeric structures within the 30 nm pores. Thus, when a TiO₂-modified electrode is exposed to a solution of a zeroth generation viologen dendrimer (with structure similar to 6 but methylated at the terminal nitrogens\(^ {23}\)), the dendrimer enters the mesopores immediately, as observed by cyclic voltammetry. However, when a dendrimer of the second or third generation of the same family is used\(^ {24}\) i.e., species with molecular diameters larger than 2–3 nm, no response from dendrimers within the mesopores is observed even after hours of exposure. Obviously, for the 2–3 nm thick dendrimers, the channels between the mesopores represent a bottle neck for the pore to pore diffusion. The same argument is expected to hold for the release of oligomeric viologen structures synthesized within the pores according to Scheme 1.

Having a stable high-resolution electrochromic working electrode in hand, a transparent counter electrode was developed that meets the optical and electrochemical requirements of the working electrode, i.e., transparency independent of the charge storage state and sufficient capacity. CeO₂ was often used as material for counter electrodes because of its Li⁺-intercalation properties but unfortunately it shows sluggish kinetics\(^ {25-27}\). The CeO₂ based electrode developed in this work consists of a mesoporous ATO (antimony tin oxide) electrode coated with CeO₂ thus combining the high surface area of a conductive carrier material with the benefits of the charge-storing capacity of the CeO₂, which is transparent and shows negligible coloration in both oxidation states. The electrode exhibits a capacity of approximately 30 mC/cm² and switching times comparable to the working electrode. Alternatively, we used a very fast, non-transparent counter electrode based on a highly doped ATO film with an additional diffusive reflective layer consisting of passivated microcrystallite TiO₂ (Figs 2.f,g) as described previously\(^ {28}\) (see also Experimental section).

Sealed transparent and reflective electrochromic cells were assembled using the described working and counter electrodes and a solvent electrolyte system such as 1 M LiClO₄ in γ-butylrolactone were assembled. To the best of our knowledge the resolution of the switchable pictures obtained is of unprecedented quality (Fig. 2). Switching times are in the range of 2 s depending on the applied potential and preliminary aging tests indicate good long-term stability. These devices show absolutely no blooming after 9 months of repetitive operation.

Inkjet printing technology (a top-down approach) has been combined with cascade-type crosslinking reactions of viologens in the mesopores of a semiconducting TiO₂ electrode (a bottom-up concept). Molecular entraping of the oligomeric electrochromophore prevents loss of sharpness due to entropy-driven broadening of the colored spots that are defined by the inkjet printing process. Moreover, a completely transpar-
Production of Submicrometer Diameter Fibers by Two-Fluid Electrospinning**

By Jian H. Yu, Sergey V. Fridrikh, and Gregory C. Rutledge*

Electrostatic fiber formation, or “electrospinning” is a process that employs electrostatic forces to produce fibers with diameters ranging from micrometers down to tens of nanometers, two to three orders of magnitude smaller than those produced by conventional fiber-spinning methods. The first patent for the electrospinning process dates back to 1934.[1] Recently, this process has attracted great attention due to the ease with which it allows the production of submicrometer diameter fibers from both synthetic and natural polymers.[2-4] The process itself is quite general; over thirty different polymers have been electrospun in batch or continuous mode to produce fibers with diameters below 1 μm.[5] Numerous and diverse applications for electrospun fibers have been proposed. These include: biodegradable electrospun nonwoven fabrics for use in tissue engineering and in drug delivery,[6,7] high-surface-area fabrics for use in protective clothing and sensors,[8,9] and highly efficient filtration membranes based on small inter-fiber distances combined with low pressure drop.[10,11] Post treatment of electrospun fibers has been used to produce ceramic or metallic nanoﬁbers.[12,13]

Despite these encouraging results, routine production of uniform fibers with diameters less than 100 nm in diameter is still a challenge. Two major strategies to decrease the fiber diameter have generally been employed. The first is to reduce...

[20] The picture to be inkjet printed on TiO2 is composed on the computer using Corel Draw 9. Monochromatic colored vector graphics were used for alphanumeric information and drawings (pure magenta). The implemented digital photography was first converted into a 360 dpi black and white (1-bit) bitmap with the black pixels set to magenta coloured vector squares using Corel Photo-Paint 9.
[22] A picture prepared with N-benzylated 1 on a mesoporous TiO2 electrode (see Experimental section). The electrode was incorporated in a sealed cell in the same way as done for the transparent crosslinked ECD (Figs. 2a–e).

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