notable candidate is Prussian Blue (iron hexacyanoferrate, or PB), whose distinctive color is due to intervalence charge transfer between Fe(II) and Fe(III), which makes thin PB films opaque. By selectively reducing the Fe(III) this mechanism is eliminated, and the thin film is bleached to a transparent state. The opacity can be recovered through oxidation.

The Nanyang team noted that the oxidation process to recover PB from a bleached state can occur spontaneously in an aqueous solution that contains dissolved oxygen. This led them to investigate the possibility of a self-recovering electrochromic device. Sun notes that "Prussian Blue is quite unique: it is one of the artificial pigments, and it can form a battery in its reducing and oxidation processes, so we realized it has a lot of potential." The key step was to identify a counter electrode that could easily lose electrons to PB. After some experimentation, the researchers selected aluminum, constructing a device based on electrodeposition of a PB film on indium-tin-oxide-coated glass, an aluminum counter electrode (only covering a small fraction of the device to avoid obstructing the light), and 3 mol/l KCl aqueous electrolyte. The device can be bleached to transparency by connecting the electrodes and reducing the Fe(III), which occurs over several tens of seconds and shows a maximum optical transparency change of 52.2% for red light (670 nm wavelength). When the electrodes are disconnected, the device spontaneously returns to opaque as the iron is oxidized by oxygen dissolved in the electrolyte. This occurs much more slowly; transparency is reduced by 38.5% after two hours. By applying a 2 V external bias, the researchers were able to significantly accelerate this transition, demonstrating 10-s cycling through +/–10% changes in transparency.

In addition to the electrochromic behavior, the researchers note that the device also functions as a "self-recoverable" battery, with an open-circuit voltage of 1.26 V. During the electrochromic bleaching process the battery is discharging, with a measured discharge capacity of 63.6 mAh/g at –2 V for 30 s. The battery then spontaneously recovers during the electrochromic recovery process; after 24 hours the battery discharges at 61.9% of the original capacity. The spontaneous cycling behavior of the device—considered as either an electrochromic window or a battery—is accompanied by the formation of $Al(OH)_3$ precipitate in the electrolyte, gradually consuming the Al electrode. However, the researchers note that the rate at which this occurs is negligible, and is unlikely to limit the device performance.

Sebastien Lounis of Lawrence Berkeley National Laboratory agrees that the need for an external bias is a significant problem for the market deployment of smart windows: "With current electrochromic technology, you're looking at involving both carpenters and electricians for installation, which creates a major headache for the builder and drives up costs." A bias-free electrochromic window could therefore help accelerate the technology into much wider use.

Prussian Blue has captivated artists and scientists since it was discovered over 300 years ago, and it is now used in everything from art to medicine to machining. But given these results, it may still have surprises in store.

**Colin McCormick**

## Giant spin-splitting revealed on $SrTiO_3$ surface

Conventional electronics is based on semiconductor materials such as silicon, germanium, or gallium arsenide, which are increasingly reaching their performance limits. One key approach to make these electronic devices faster and more efficient is spintronics, which requires new materials. Scientists have had their sights on oxides such as strontium titanate ($SrTiO_3$) as an alternative to the well-established semiconductors. A thin conductive layer forms on the pure surface of $SrTiO_3$—a two-dimensional electron gas (2DEG), where electrons can virtually move freely, like gas particles. Milan Radović and his colleague Nicholas Plumb at Paul Scherrer Institute have now measured the properties of the electrons in this 2DEG, providing the clearest description of the electronic structure of the metallic surface state on $SrTiO_3$ to date. It is characterized by a band structure, which can be imagined as a multilane motorway for electrons. On each lane, the electrons possess certain properties, such as a specific spin direction or certain energy levels.

To study the spin of the 2D electrons in more detail, spin and angular-resolution photoemission measurements (SARPES) were performed with colleagues from EPFL Switzerland and CSNSM, Université Paris-Sud, France. The results showed that these 2D electrons are located in two subbands and that the majority of the electron spins are aligned parallel to the surface in both bands. In one band, however, their orientation rotates clockwise, in the other counterclockwise.

While the researchers had expected this helical spin structure, they were surprised to find two separate subbands with spins oriented in opposing directions. They were also surprised to find that a relatively large amount of energy (100 meV) is required to allow the electron transition from one band to the other. The researchers refer to a sizeable bandgap, which is around 10 times larger than in other known systems up to now.

So far, however, this effect has only been observed under ultrahigh vacuum conditions. Whether it can be achieved on the same scale under practical conditions remains to be seen.

The scientists published their results in the August 18 issue of *Physical Review Letters* (DOI: 10.1103/PhysRevLett.113.086801) and the October 12 issue of *Nature Materials* (DOI: 10.1038/NMAT4107).

**Uta Deffke**


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