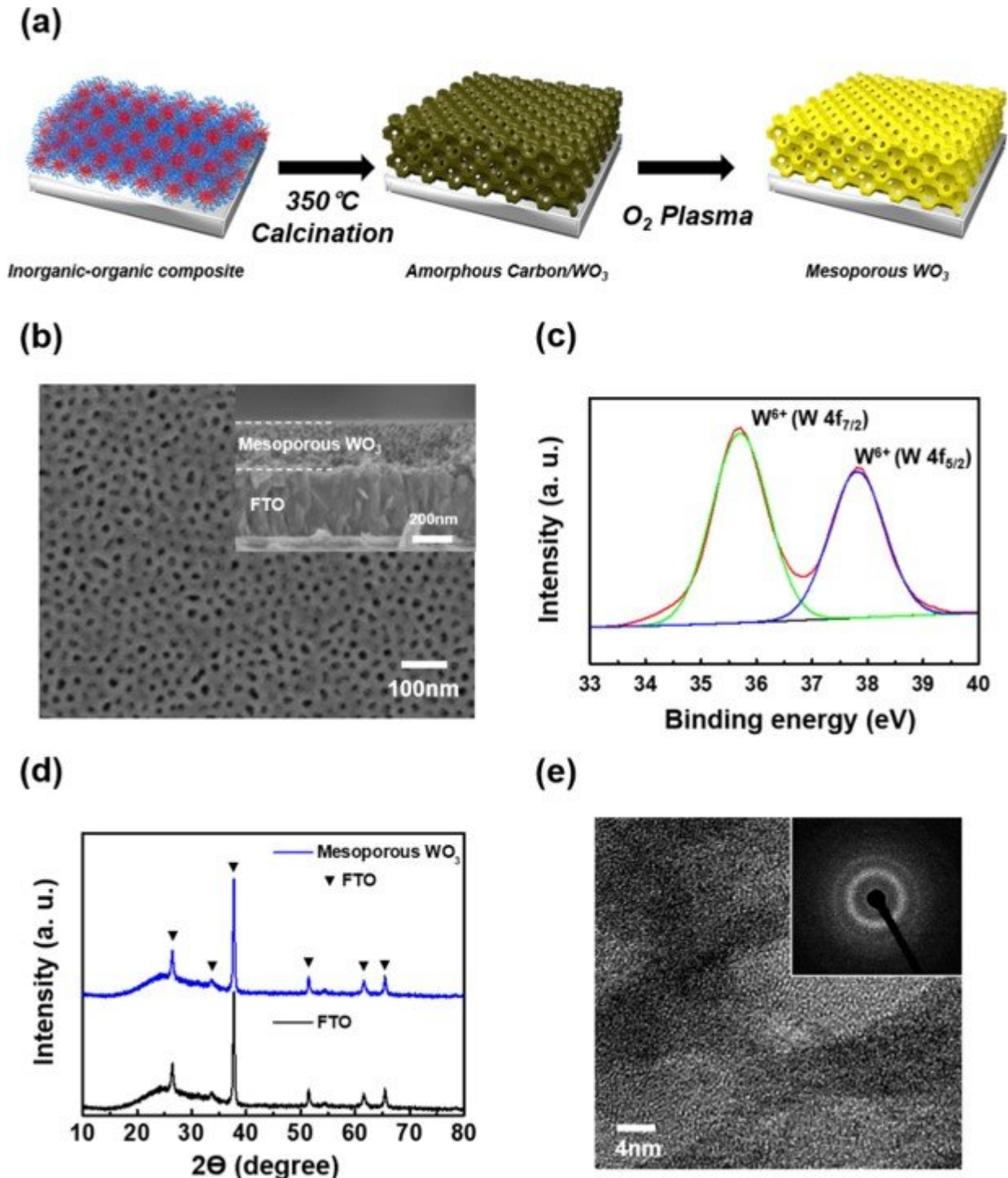


# Extremely fast electrochromic supercapacitors

January 7 2021, by Thamarasee Jeewandara

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Fabrication and characterization of mesoporous  $\text{WO}_3$  films. (a) Schematic showing the fabrication process of the mesoporous  $\text{WO}_3$  film. (b) Scanning electron microscopy (SEM) image (top view) of the mesoporous  $\text{WO}_3$  film (inset: cross-sectional view). (c) W 4f XPS spectra of the mesoporous  $\text{WO}_3$  film.

d XRD patterns of the mesoporous WO<sub>3</sub> film and bare FTO glass. e HR-TEM image of the mesoporous WO<sub>3</sub> film (inset: SAED pattern). Credit: NPG Asia Materials, doi: 10.1038/s41427-020-00257-w

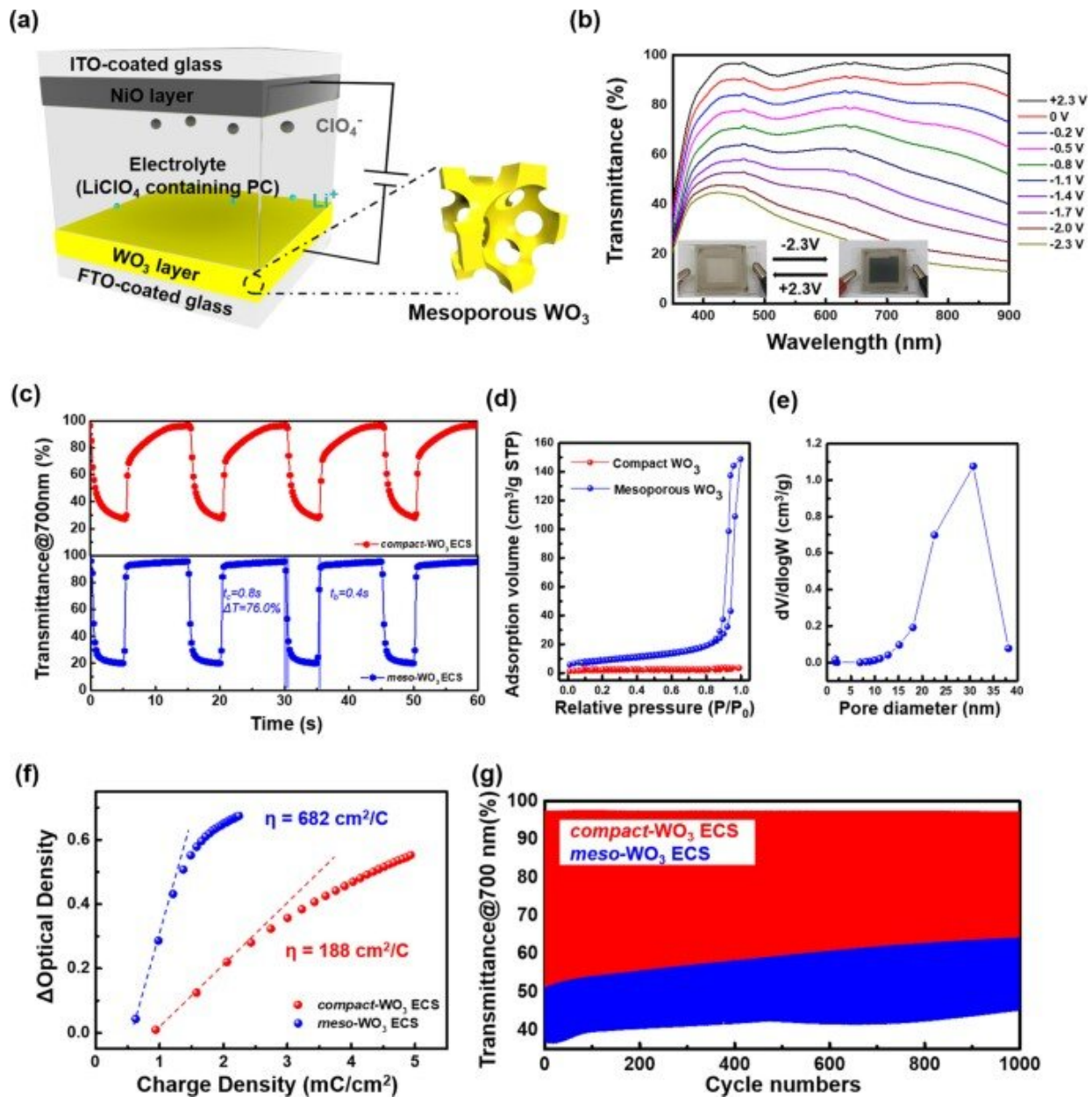
During materials engineering, a network of tiny holes or pores can improve the energy storage capacity of materials for applications as [smart windows](#). Smart windows are platforms whose light transmission properties can be altered when light, voltage or heat is applied. Scientists can control the fraction of light passing through the material using an electrical voltage to electrically switch from transparent to opaque materials during charge transfer. While this feature is associated with storage and release of energy, the same materials can be used for energy storage as well. In a new report, Jeon-Woo Kim and a team of scientists at the Pohang University of Science and Technology in South Korea developed and improved electrochromic supercapacitors made from [tungsten trioxide](#) (WO<sub>3</sub>). They used an evaporation-induced self-assembly process to deposit a film of tungsten trioxide with pores, where the porous architecture increased the speed of switching and [capacitance](#) in the material compared to conventional tungsten trioxide thin films. The work is now published on *Nature Asia Materials*.

## Photonics: smart windows and energy storage

During this work, Kim et al. demonstrated the ultrafast response of [electrochromic](#) supercapacitors by exploring the mesoporous structure of the constituent materials. Electrochromic devices (ECDs) can [generate reversible color changes](#) that correspond to electricity with promising applications across smart windows, displays and military camouflage. The devices can also control light transmittance to build materials for climate adaptive [energy-efficient buildings](#). The functionality of ECDs can be extended to [energy storage devices](#) known as [electrochromic](#)

[supercapacitors](#) (ECS). Such supercapacitors are increasingly under investigation as [next-generation electrochemical components](#) capable of changing their own optical properties and storing the energy supplied. Their inherent optical characteristics can therefore directly reveal the [real-time energy levels](#) stored within. Researchers had developed such high-performance devices using electrochromic chromophores based on transition metal oxides such as tungsten trioxide due to their [superior electrochemical properties](#). The electrochromic displays developed here can change color based on their stored levels of energy and the product will have broad implications as next-generation smart window materials for buildings and portable energy storage.

## **Developing the new materials and building the device**



Electrochromic (EC) performance of meso- and compact-WO<sub>3</sub> electrochromic supercapacitors (ECSs). (a) ECS structure employed in this work. (b) Transmittance spectra of the meso-WO<sub>3</sub> ECS as a function of applied voltages (inset: photographs of the colored and bleached states). (c) In situ optical responses of the compact-WO<sub>3</sub> ECS (red line) and the meso-WO<sub>3</sub> ECS (blue line). (d) Nitrogen adsorption-desorption isotherm curves of the mesoporous and compact WO<sub>3</sub>. (e) Pore size distribution of mesoporous WO<sub>3</sub>. (f) Optical density variation as a function of injected charge density. (g)

Coloration/bleaching cycling stability of the two ECSs for 1000 cycles. Credit: NPG Asia Materials, doi: 10.1038/s41427-020-00257-w

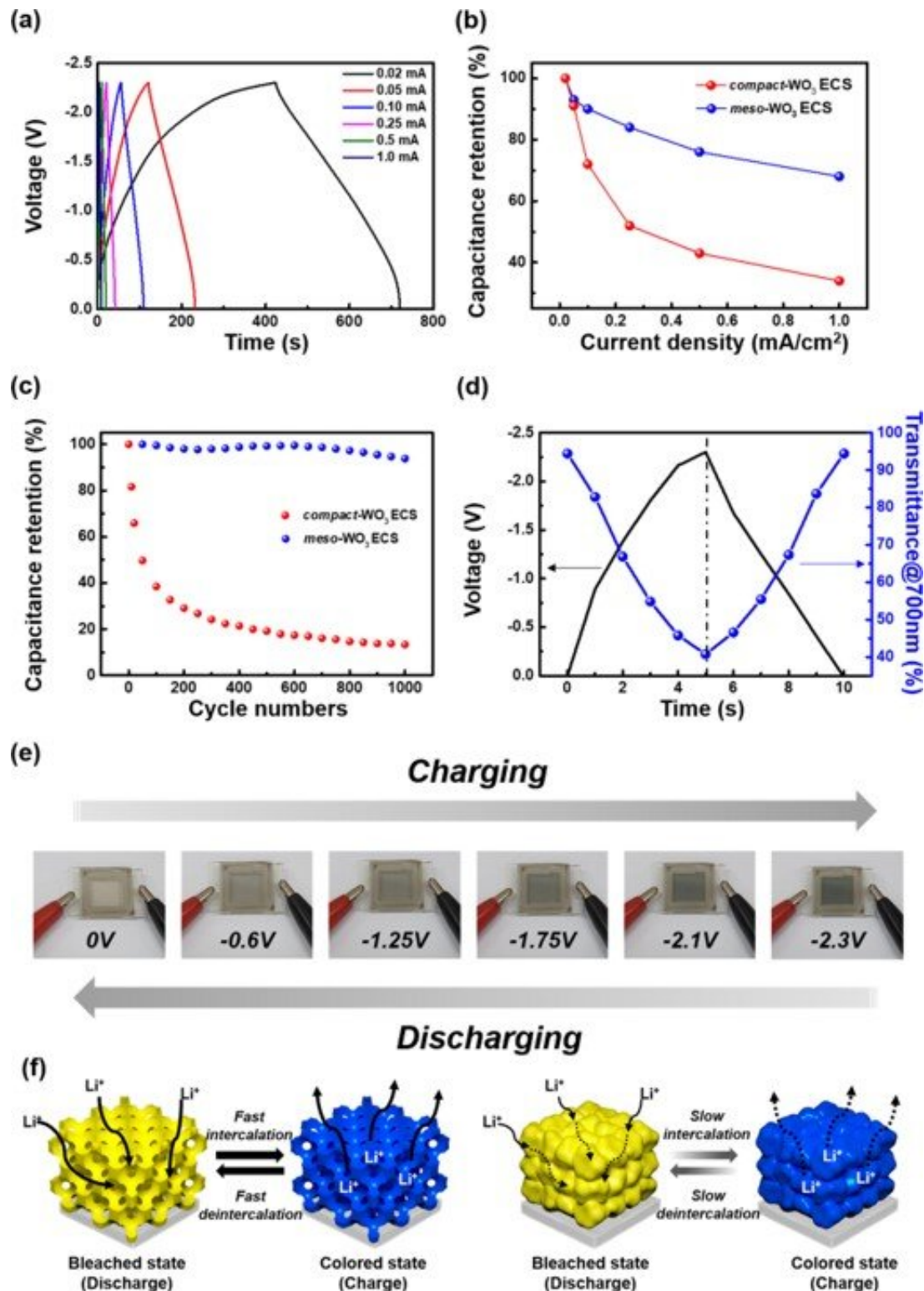
The scientists detailed the fabrication process using a mixed solution of [tetrahydrofuran](#) and [polystyrene-\*block\*-polyethylene oxide](#) and ethanol-based [tungsten hexachloride](#) ( $\text{WCl}_3$ ) as a precursor of tungsten trioxide. The resulting film contained inorganic-organic composites. They then calcinated the composite to partially remove the organic components and transform the remainder to amorphous carbon. The inorganic components underwent condensation to form tungsten trioxide and the resulting composite film contained a carbon/tungsten trioxide structure. The team subsequently exposed the film to oxygen plasma to eliminate the amorphous carbon, which they confirmed using [Raman spectroscopy](#). Using [scanning electron microscopy](#) (SEM), the scientists supported the mesoporous structure of the resulting tungsten trioxide ( $\text{WO}_3$ ) film with small pores (less than 30 nm) and a thickness approximating 250 nm.

Kim et al. expected ultrafast dynamics with mesoporous  $\text{WO}_3$ -based electrochromic supercapacitors (denoted *meso*- $\text{WO}_3$ -ECs), and for comparison, they also developed a compact [device](#) denoted *compact*- $\text{WO}_3$ -ECs using  $\text{WO}_3$  nanoparticles. Thereafter they recorded the [UV-vis transmittance spectra](#) at various applied voltages to understand the electrochromic behavior of the two devices. When the applied voltage increased, the transmittance gradually decreased across the entire range of visible light wavelengths due to redox reactions in the setup. The team could then recover the transparent bleached state of the device by applying a 2.3 voltage.

## Comparing device functionality

To compare the electrochromic dynamic response of the two devices,

Kim et al. recorded the transmittance profiles at 700 nm, and at alternating potentials. The *meso*-WO<sub>3</sub>-ECS device showed large optical modulation and ultrafast coloration in 0.8 seconds and a bleaching time of 0.4 seconds, notably faster than previous reports. The team did not obtain a similarly stable state of coloring and bleaching under the same conditions with *compact*-WO<sub>3</sub>-ECS. The results depended on the surface area of the devices, where the *meso*-WO<sub>3</sub>-ECS device consumed less energy compared to the *compact*-WO<sub>3</sub>-ECS.



Energy storage characteristics of meso- and compact-WO<sub>3</sub> ECSs. (a) Galvanostatic charging/discharging (GCD) curves of the meso-WO<sub>3</sub> ECS at various current densities. (b) Dependence of the capacitance retention of the



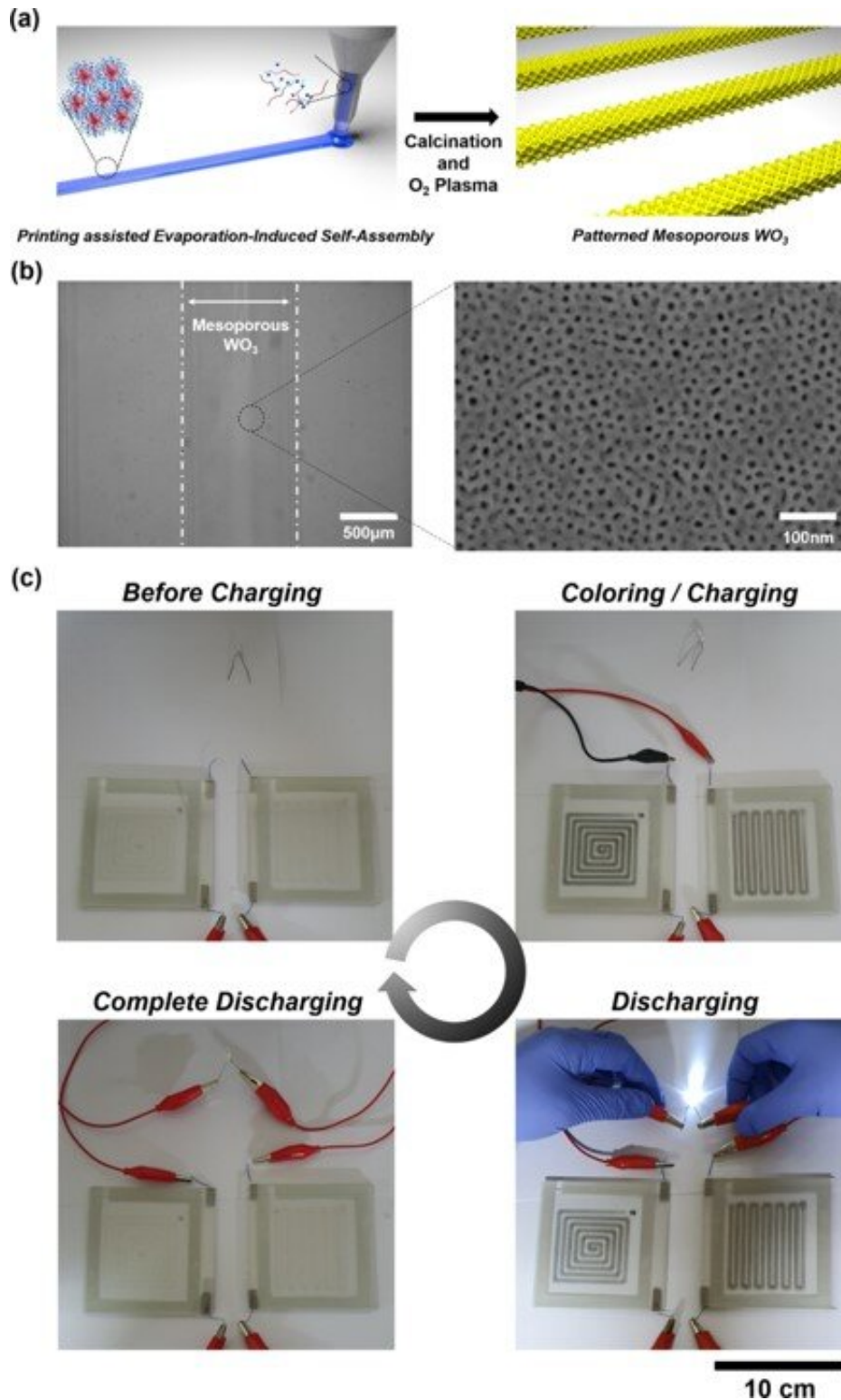
compact- and meso-WO<sub>3</sub> ECSs on the charging/discharging current densities. (c) Charging/discharging cycling stability of the ECSs at a current density of 1.0mA/cm<sup>2</sup>. (d) GCD curve at 1.0mA/cm<sup>2</sup> and the corresponding in situ transmittance profile at 700nm for the meso-WO<sub>3</sub> ECS. (e) Photographs of the meso-WO<sub>3</sub> ECS during the charging and discharging process. (f) Schematic illustration of the ion intercalation in meso- (left) and compact-WO<sub>3</sub> (right). Credit: NPG Asia Materials, doi: 10.1038/s41427-020-00257-w

Typically, electrochromic supercapacitor devices must maintain cycling stability under fast response conditions. Additional tests under quick switching conditions between coloration and bleaching for 1000 cycles therefore showed how the mesoporous device retained 85.5 percent of their original optical modulation, while the optical modulation of compact devices dropped. The team credited the excellent stability of the mesoporous device to its characteristic architecture with a large surface area, well-suited for dynamic applications that require a fast response.

## Charge transfer dynamics

Kim et al. next compared the charge transfer and ion kinetics of the devices and the results showed a smaller [contact resistance](#), smaller [charge transfer resistance](#) and lower [ion diffusion resistance](#) for the mesoporous devices. The devices showed significantly different charge-storing capabilities as the functional current density increased. The work implied the mesoporous supercapacitors to be more promising compared to the compact devices to form quick charging and discharging devices with outstanding long-term stability. The team then directly viewed the stored energy levels of the supercapacitors. The mesoporous device showed no significant degradation of optical contrast, which they credited to its effective and fast ion transport properties. With compact

devices, the optical modulation dramatically decreased while the current density increased, the compact devices were therefore not as efficient for high-rate functionality due to their inefficient ion transport and slow charge transfer.



Application of combined printing evaporation-induced self-assembly (PEISA) for the fabrication of functional ECSDs. (a) Schematic illustration of PEISA. (b) OM (left) and SEM (right) images of mesoporous WO<sub>3</sub> fabricated by PEISA.

(c) Photographs of the ECSD during the reversible charging (coloration of the pattern) and discharging (LED light on and bleaching) test. For this application, two ECSDs were connected in series. Credit: NPG Asia Materials, doi: 10.1038/s41427-020-00257-w

## **Printing and evaporation-induced self-assembly**

The team then combined printing and evaporation-induced self-assembly to develop the highly functional, energy-storing, electrochromic supercapacitor displays. This printing process produced a micellar structure through the nozzle after evaporation, which they then subjected to sequential calcination and oxygen plasma treatment to form a patterned mesoporous  $\text{WO}_3$  device for energy-storing applications. When they charged the device, the patterns turned dark blue to indicate the charged state. To prove its mechanism of action, the team connected the device to a white-light emitting diode (LED) that initially emitted light, when the stored energy was consumed, the device returned to its original transparent state.

## **Outlook: next-generation smart electronics.**

In this way, Jeon-Woo Kim and colleagues developed multifunctional electrochromic supercapacitors based on amorphous mesoporous  $\text{WO}_3$  films. Compared to the compact version of electrochromic supercapacitors (*compact- $\text{WO}_3$ -ECS*), the mesoporous electrochromic supercapacitors (*meso- $\text{WO}_3$ -ECS*) showed superior performance. The scientists credited this to its large surface area and amorphous nature. The mesoporous devices functioned rapidly to serve as electrochemical reflective displays and to store electrical charge. This setup can also power other electronic devices, as the color intensity of the pattern on the device indicated the level of stored energy within. The outcomes will

have tremendous potential to form next-generation smart electronics.

**More information:** Keon-Woo Kim et al. Extremely fast electrochromic supercapacitors based on mesoporous WO<sub>3</sub> prepared by an evaporation-induced self-assembly, *NPG Asia Materials* (2020). DOI: [10.1038/s41427-020-00257-w](https://doi.org/10.1038/s41427-020-00257-w)

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