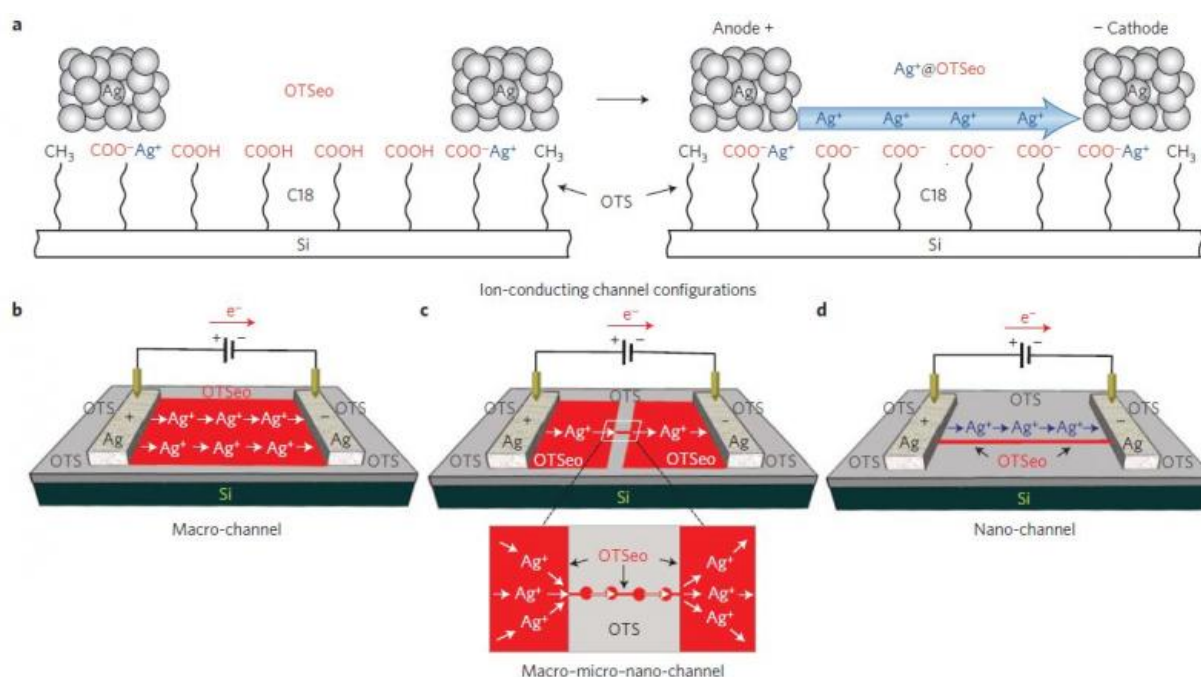


Nanoionics: A versatile system for constructing ion-conducting channels on monolayers

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Schematic representation (not to scale) of proposed bias-driven ionic transport in the different ion-conducting pattern configurations investigated in this study.

Credit: (c) *Nature Materials*, doi: 10.1038/nmat4254

(Phys.org)—Nanoionics is a sub-field of nanotechnology that is concerned with nanoscale phenomena involving migration of ions in solid maters. Thus far, however, the confinement of ionic currents to

predefined paths in a manner resembling the motion of electrons in wires of electronic conductors has not been explored.

To that end, Jonathan Berson, Doron Burshtain, Assaf Zeira, Alexander Yoffe, Rivka Maoz, and Jacob Sagiv from the Department of Materials and Interfaces at the Weizmann Institute of Science in Israel have developed a proof-of-concept approach to making custom-designed ion-conducting surface patterns using constructive lithography and organosilane self-assembled monolayers, applicable to various metal ions. Their work is reported in *Nature Materials*.

Constructive lithography involves an electrochemical oxidative reaction between a conductive atomic force microscope (AFM) tip and the molecules attached to a silicon wafer, typically as monolayers. This allows for a level of precision in which one can select which molecules will undergo the reaction and which ones will not. In this study, organosilane monolayers comprised of Si-Cl₃ anchors, an aliphatic carbon backbone, and a methyl (-CH₃) terminal group are selectively oxidized using constructive lithography. The methyl terminal group is oxidized to a carboxylic acid terminal group (-COOH), without changing the backbone and anchor.

Constructive lithography allows for the creation of sharp boundary points. These boundaries are between surface regions populated by methyl-terminated molecules and those populated by carboxylic acid-terminated molecules. Electrodes of a given metal can be placed on the [carboxylic acid](#)-terminated surface regions at such boundary sites, thus setting up a carboxylic pathway for ions to travel.

For the initial model system in this research, Berson and Burshtain, et al. placed [silver](#) (Ag) [electrodes](#) at boundary sites, and then ran d.c. voltage through the electrodes, thus producing mobile silver ions. Their goal was to see if the Ag⁺ ions would coordinate to the deprotonated carboxylic

acids, essentially traversing the length of the specified pathway from anode to cathode without the use of an added electrolyte.

Fourier Transform Infrared spectroscopy (FTIR) verified that the targeted terminal $-\text{CH}_3$ groups converted to $-\text{COOH}$ without disturbing the other segments of the monolayer. Furthermore, FTIR readings were taken over a period of time while a d.c. voltage of 1 mV to 100 mV was applied. This confirmed that $-\text{COOH}$ lost its proton forming the silver carboxylate salt. XPS confirmed that the silver ions followed the carboxylate pathway located between the two electrodes and did not interact with the methyl-terminated molecules. Resistance studies elucidated the transport of ions across channels of varying lengths and widths.

The same procedure was followed with titanium electrodes instead of silver electrodes. Berson and Burshtain et al. looked at a system with titanium electrodes serving as the anode and the cathode, and a combination system with silver and titanium electrodes. FTIR confirmed the presence of Ti^{4+} on the surface of the system with titanium electrodes. The mixed electrode system showed evidence that one cation can replace the other one on the carboxylate surface while competing for available $-\text{COO}^-$ sites.

Arrhenius plots of the silver and titanium system indicate that a similar conduction mechanism occurs in the mixed metal system compared to the single metal system. There is a difference between titanium's activation energy compared to silver, which the authors believe is likely due to Ti^{4+} coordinating to four $-\text{COO}^-$ molecules compared to Ag^+ coordinating to one. Furthermore, Ti^{4+} bonding takes on a slightly more covalent character than Ag^+ .

While the aforementioned studies were done at the macroscale, the next step was to see if the model system would work with nano-channel

configurations. The authors constructed a system with two macro-channels that were separated by a nano-channel with silver electrodes residing in the macro-channels and another system in which the silver electrodes were on either side of a nano-channel.

Resistance calculations and AFM images indicated that the system with two macro-channels separated by a nano-channel behaved similarly to the macro-channels. However, when the electrodes were placed on the boundaries of the nano-channel, a thin film of silver accumulated along the channel instead of at the cathode, likely due to higher flux density of ions in the system and therefore more opportunity for nucleation and subsequent silver filament growth along the nano-channel pathway.

This research demonstrates the ability to tailor ion-conducting conductive channels using constructive [lithography](#) on alkyl silane monolayers. This technique is versatile in that the conductive channels may accommodate different mobile ions produced by using different metals can be used for the electrodes.

According to Dr. Sagiv, "This research demonstrates the possible realization of a conceptually new type of generic solid ionic material that may be shaped ion ion-conducting channels with predefined lengths, widths, and trajectories, suitable for planned transport of different selected cations over distances spanning nanoscale-to-macroscale dimensions." Furthermore, he says that the broader implications of this research "are expected to enable fabrication of task-designed ionic circuits and fast ionic switches applicable in future devices based on novel modes of information processing and storage."

More information: "Single-layer ionic conduction on carbonyl-terminated silane monolayers patterned by constructive lithography" *Nature Materials*, [DOI: 10.1038/nmat4254](https://doi.org/10.1038/nmat4254) .
[www.nature.com/nmat/journal/va ... t/full/nmat4254.html](http://www.nature.com/nmat/journal/va...t/full/nmat4254.html)

Abstract

Ionic transport plays a central role in key technologies relevant to energy, and information processing and storage, as well as in the implementation of biological functions in living organisms. Here, we introduce a supramolecular strategy based on the non-destructive chemical patterning of a highly ordered self-assembled monolayer that allows the reproducible fabrication of ion-conducting surface patterns (ion-conducting channels) with top -COOH functional groups precisely definable over the full range of length scales from nanometre to centimetre. The transport of a single layer of selected metal ions and the electrochemical processes related to their motion may thus be confined to predefined surface paths. As a generic solid ionic conductor that can accommodate different mobile ions in the absence of any added electrolyte, these ion-conducting channels exhibit bias-induced competitive transport of different ionic species. This approach offers unprecedented opportunities for the realization of designed ion-conducting systems with nanoscale control, beyond the inherent limitations posed by available ionic materials.

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