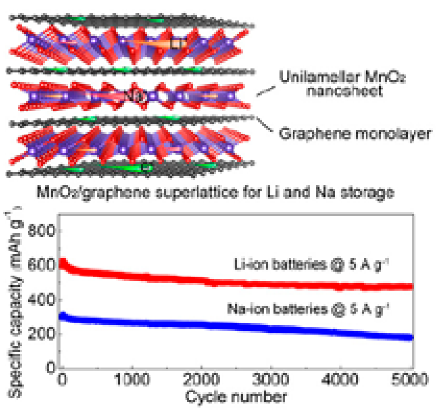
METAL OXIDE/GRAPHENE NANOSHEET EXHIBITS UNPRECEDENTED ENERGY STORAGE PROPERTIES

Single-layer metal oxide nanosheets sandwiched between graphene layers exhibit record energy storage figures of merit.

The unique physical properties of nanomaterials are important for the realization of high performance energy storage devices. For example, the ultra-narrow spaces between multilayered two-dimensional (2D) nanosheets are suitable for high efficiency ion intercalation, namely, reversible insertion of ions into the spaces between layers. Importantly, single-layer nanosheets with nearly ideal atomic-scale thickness exhibit short diffusion distances and large numbers of active sites—properties that are essential for fabricating electrode materials of high performing energy storage devices.

However, despite extensive research on 2D materials such as graphene and transition metal dichalcogenides, the energy storage capacity has not met expectations. More recently, research has also turned to explore 2D metal oxides—materials with many more exposed active sites, and even shorter diffusion lengths. The main issues to resolve include synthesis of genuine single layered metal oxides, prevention of 'restacking' during chemical processes to fabricate electrodes, and improving their electrical conductivity.



STRUCTURE OF MnO_2/GRAPHENE SUPERLATTICE-LIKE STRUCTURE

Here, a group led by Takayoshi Sasaki at WPI-MANA reported the synthesis of superlattice-like MnO_2/graphene 2D nanostructures that exhibited the best figures of merit for energy storage reported to-date.

The researchers synthesized the MnO_2/graphene superlattice structures by 'electrostatic assembly' of single-layer MnO_2 and graphene in a solution, exploiting the differences in the charge states of the respective materials: The MnO_2 nanosheets are negatively charged and modified reduced graphene oxide (rGO) nanosheets are positively charged. The two important points about this fabrication process and the resulting nanosheet superlattices are that the MnO_2 nanosheets were 'genuine unilamellar' structures and each of the MnO_2 nanosheets was 'stabilized' between the atomic layers of graphene.

The MnO_2/graphene nanostructures were used as anodes for Li and Na ion batteries. Electrochemical measurements showed specific capacities of 1325 and 795 mAh/g at 0.1 A/g and 370 and 245 mAh/g at 12.8 A/g for Li and Na storage, respectively. "More importantly, an ultralong cyclability with 0.004% and 0.0078% capacity decay per cycle up to 5000 cycles was achieved for Li and Na storage, respectively, outperforming previously reported metal oxide-based anodes to date," state the authors.

"The superlattice composite material described in this paper is based on MANA's concept of 'Materials Nanoarchitectonics', says Sasaki. "We have taken two types of 2D materials with differing properties and formed an advanced composite material with synergistic characteristics that are not exhibited by a single material." ■

REFERENCE

PAN XIONG, RENZHI MA, NOBUYUKI SAKAI, AND TAKAYOSHI SASAKI, GENUINE UNILAMELLAR METAL OXIDE NANOSHEETS CONFINED IN A SUPERLATTICE-LIKE STRUCTURE FOR SUPERIOR ENERGY STORAGE, ACS NANO, 12 ,1768–1777, (2018).

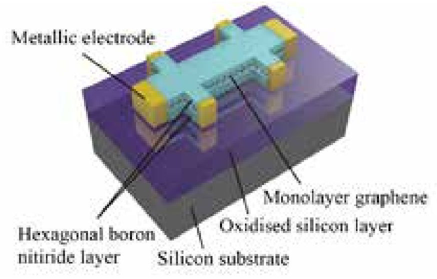
EVIDENCE OF A NEW TYPE OF QUANTUM EFFECT

The quantum Hall effect (QHE) is a phenomenon that can occur in a two-dimensional electron gas — a system in which electrons can move in a plane but not perpendicularly to it. Such a system is typically realized in a heterostructure of thinly stacked layers of different semiconductors. The QHE is usually observed at low temperatures and high magnetic fields; it manifests itself through the quantization of values of the electronic conductance (the inverse of resistance) — the values are integer or particular fractional multiples of a fundamental conductance quantum.

Recently, variants of the QHE have been discovered, such as the quantum spin Hall and the anomalous quantum Hall effect. Now, Satoshi Moriyama at WPI-MANA, NIMS, Tsukuba, Japan, and colleagues have observed yet another relative of the QHE: the quantum valley Hall effect.

The notion of 'valleys' refers to electronic states having the same energy but a different crystal momentum; the states are said to lie in different valleys. A new type of electronics called 'valleytronics', based on the valley degree of freedom, is being researched since some years.

Moriyama and colleagues demonstrated the quantum valley Hall effect in a special heterostructure capable of hosting a two-dimensional electron gas: a sheet of graphene sandwiched between hexagonal



DEVICE STRUCTURE

boron nitride (h-BN) layers. Graphene is a one-atom thin layer of carbon atoms forming a honeycomb pattern. h-BN is similar; it is also a monolayer with a honeycomb structure, but it has a slightly different lattice parameter. Due to the mismatch in lattice size, the periodicity of the combined system is much larger — overlaying the two lattices results in a moiré pattern.

Importantly, the investigated electronic regime in the superlattice was ballistic: the electrons' mean free path (the mean distance travelled between scattering events) was estimated to be 1 to 2 micrometer, which was comparable to the size of the sample.

The researchers varied the magnetic field while measuring resistances, and at a small interval centered around zero field they observed a non-vanishing resistance — a signature of the quantum valley Hall state.

An important fundamental finding on its own, Moriyama and colleagues note that it also may lead to potential applications: "[such] unconventional magnetism should have the potential for engineering the energy-band structure [of devices] even with a weak magnetic field as well as for spintronics applications." ■

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K. KOMATSU ET AL., "OBSERVATION OF THE QUANTUM VALLEY HALL STATE IN BALLISTIC GRAPHENE SUPERLATTICES", SCI. ADV. 4:EAAQ0194 (2018).

IONIC DEVICES LEARN HOW TO MAKE DECISIONS

Decision-making processes require the examination of complex data in order to effectively adapt to dynamic changes in the environment and make decisions about the most appropriate way to behave. Emulating these processes with computers requires enormous resources, so new avenues need to be explored.

Now, writing in Science Advances, Takashi Tsuchiya, Tohru Tsuruoka, Song-Ju Kim (currently at Keio Univ.), Kazuya Terabe and Masakazu Aono at the WPI-MANA, NIMS, Tsukuba, Japan propose to use ionic devices to perform decision-making operations. They apply their

devices, named ionic decision-makers, to the solution of Multi-armed Bandit Problems (MBPs); mathematical problems in which a gambler given a choice of slot machines must select the appropriate machines to play so as to maximize the total reward in a series of trials. MBPs have been applied to various practical technologies related to artificial intelligence. The scenario investigated by the authors is that of a user of busy communication channels who needs to select a channel to transmit information with maximum efficiency.

A two-electrode electrochemical cell, with Nafion proton conducting polymer electrolyte and Pt electrodes, is used to solve MBPs with two channels (A and B), with transmission probabilities P_A and P_B, of which the user has no a priori knowledge. The setup comprises the cell, a device controlling the flow of electric current through it, and a random number generator that determines the transmission of data packets. The electrical potential of each of the two electrodes, A and B, is used to evaluate which channel is the best to select, and it increases or decreases on the basis of whether or not the channel is open for transmission.

Ions in the electrolyte are initially randomly distributed, but there is still a small voltage across the device. This voltage is measured; if it is positive (negative), a random number is generated to emulate the selection of channel A (B), that is, to determine whether a packet is transmitted or not. In accordance with the result, a pulse current is then applied in the corresponding polarity, varying the concentration of ions and/or molecules in the vicinity of the electrodes. The rate of correct selection increases with the number of selections, because the variation in the concentration near the electrodes makes it a more or less likely choice in subsequent selections. To verify the adaptability of the system to environmental changes, P_A and P_B was inverted after some selections; the rate of correct selections initially dropped, but the decision maker quickly adapted.

A more complex problem is that of two network users trying to select an available channel. If they select the same channel the probability of it being open is split between them, so that the number of transmitted packets decreases substantially for both. This is an important practical problem for communication network systems with limited channels and many users. The authors present an extended decision maker, with two electrochemical cells and three channels, which is particularly effective at solving such problem and can maximize the number of packets for all users.

The authors comment, "The ionic decision-maker creates a new research field of 'materials decision-making' in which the intrinsic properties of materials are used to make decisions, not only for large-scale computations of human behavior but also for developing autonomous intelligent chips for mobile applications." ■

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