A Photothermoelectric Effect in Graphene

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APPLIED PHYSICS

A Photothermoelectric Effect in Graphene

A curious response of graphene to light and heat may be useful for optoelectronic applications.

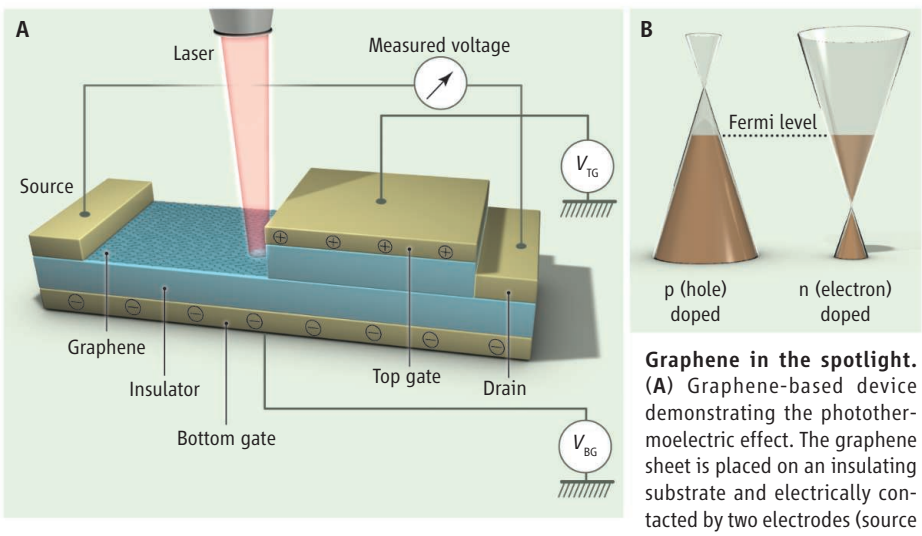
Denis Basko

A conventional thermocouple consists of two different metal wires placed in contact with each other. When the junction is heated and the free ends are kept cold, a voltage can be measured across the two free ends. If the metals are the same, then no voltage should appear. On page 648 of this issue, Gabor *et al.* (*1*) report a thermocouple effect that contradicts this conventional expectation. Upon heating a junction made of a single graphene sheet by shining laser light on it, they found that a voltage does develop across the junction. The observed photothermoelectric effect could be potentially exploited in novel optoelectronic devices.

When electrons move through a metal, they carry electric charge and energy. The former is responsible for the electric current, the latter for the heat current. The electric current is determined by the total number of electrons moving from one electrode (source) to the other (drain). The heat current depends also on how the electrons are distributed among energy levels within the metals. Because both have the same physical origin—namely, the motion of electrons through the metal—they are closely related. One manifestation of this is the Wiedemann-Franz law, an empirical observation that the ratio of electric and thermal conductivity is a constant. Another manifestation is the thermoelectric effect, whereby a temperature difference across a sample leads to the development of a voltage. Indeed, temperature difference produces a heat current, accompanied by electric current (carried by the same electrons), that is proportional to the voltage. The ratio between the voltage developed and the temperature difference is called the thermopower or Seebeck coefficient, which depends on the material. If a junction of two metals is heated up, a voltage is generated in each metal. The net voltage across the sample is nonzero if the two samples have different Seebeck coefficients, but is zero if they are the same.

Gabor *et al.* used a single sheet of graphene and placed two regions of it under different conditions such that they had different Seebeck coefficients. This is possible because the density of electrons in graphene can be strongly modified by placing an external gate electrode nearby and applying a constant voltage to it—the field effect. Although there is no electrical contact between the gate and the graphene sheet, the electric field from the gate penetrates the graphene, which then either pushes electrons away or attracts more electrons, depending on the sign of the gate voltage. In ordinary metals, this field effect does not work because the external electric field is screened at short distances (on the order of one atomic length), and because charge and heat transport occur in the bulk of the metal and therefore remain unaffected by the external field. But graphene is atomically thin, permitting a giant field effect whereby the electrical conductivity can be changed by orders of magnitude by tuning the gate voltage (*2*). A change in conductivity implies a change in the Seebeck coefficient (*3*), as was confirmed experimentally for the specific case of graphene (*4*). At room temperature, the observed variation of the Seebeck coefficient amounted to a few tens of microelectron volts per kelvin, which is at least an order of magnitude higher than for a junction between two conventional metals (gold, silver, copper) and of the same order as for alloys used in thermocouples (chromel, alumel, constantan). In addition to this large value, the crucial advantage of graphene is that the electrical and thermal properties can be controlled by an external gate voltage.

By using two gate electrodes with different voltages, two regions of the graphene sheet can be produced with different electron densities (see the figure). The junction of the two regions is heated up by a focused laser beam. Thus, the voltage appears upon exposure of the sample to light—a photovoltaic effect. In that case, is the device a photodiode rather than a thermocouple? In a conventional photodiode, illumination of a semiconductor p-n junction excites electrons (negative-charge carriers) and holes (positive-charge carriers), which are then pulled on the opposite sides of the junction by the electric field present at the junction. The spatial separation of negative and positive charges results in a photovoltage. Which mechanism is responsible for the photovoltage measured by Gabor *et al.*? A similar question has been addressed for a junction



Graphene in the spotlight. (**A**) Graphene-based device demonstrating the photothermoelectric effect. The graphene sheet is placed on an insulating substrate and electrically contacted by two electrodes (source and drain). Below the substrate, a bottom-gate electrode is placed under the whole graphene sheet. Above the right half of the sheet, separated by an insulating barrier, the top-gate electrode is placed. The electron density on the left is controlled by the bottom-gate voltage, and the density on the right by a combination of the top- and bottom-gate voltages, allowing for independent control of the densities. The junction between the two regions is illuminated by laser light, and the voltage difference between source and drain is measured. (**B**) A schematic of the electronic dispersion in the two regions of the graphene sheet (two Dirac cones that are vertically shifted to align the Fermi level).

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between single-layer graphene and bilayer graphene (*5*), where the two mechanisms would result in opposite signs of the photovoltage, and the one corresponding to the thermoelectric mechanism was observed. In the doubly gated monolayer graphene of Gabor *et al*., for the field-induced carrier separation the sign of the photovoltage would be simply determined by which of the two regions has the higher electronic density. In contrast, the thermoelectric mechanism would result in a peculiar six-fold photovoltage pattern (*6*), as was observed by Gabor *et al*.

The efficient design of an optoelectronic device requires an understanding of the main mechanism of the photovoltage generation in that device. Identification of the photothermoelectric effect as such a mechanism for graphene (*1*, *5*), together with the demonstration of external control (*1*), thus provides an opportunity to develop graphene-based optoelectronic devices.

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CELL BIOLOGY

Growth Signaling from Inside

Sensing of amino acids inside lysosomes by a proton pump initiates a chain of events that stimulates cell growth.

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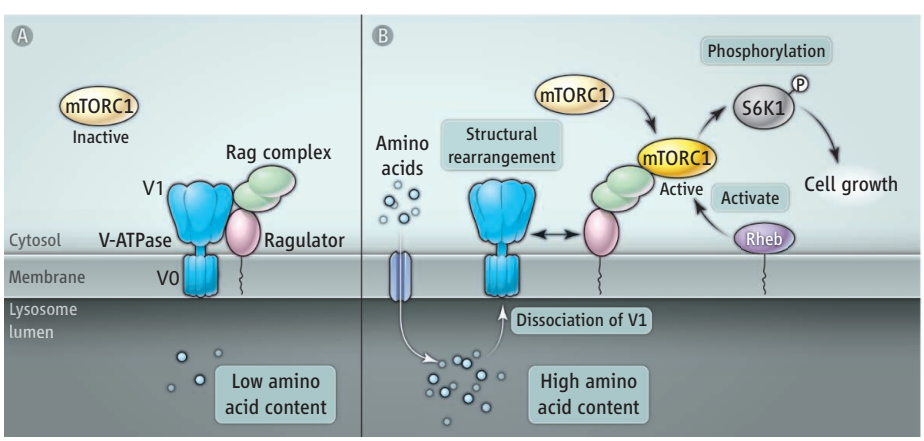
All cells have the ability to sense whether nutrients are scarce or abundant so that appropriate anabolic or catabolic programs can be initiated. A key sensor of nutrient status in eukaryotes is target of rapamycin (TOR) (*1*), an enzyme that phosphorylates a subset of proteins that function in cell growth and metabolism (*2*). In mammalian cells, TOR associates with accessory proteins to form mammalian TOR complex 1 (mTORC1) (*3*). Amino acids are potent activators of mTORC1 (*4*, *5*), but it has not been clear how mTORC1 senses amino acids within the cell. On page 678 of this issue, Zoncu *et al.* (*6*) describe how sensing amino acids occurs inside the lumen of lysosomes, the main degradative organelles in the cell.

Lysosomes are characterized by their acidity and content of degradative enzymes (*7*). Earlier work indicated that physical contact between mTORC1 and its activator, Rheb (*8*), at the lysosome determines whether amino acids can activate mTORC1 (*9*). Zoncu *et al*. therefore reasoned that lysosomes must play an important role in the amino acid–mediated activation of mTORC1. By using cultured cells from fruit flies and reducing the expression of genes with known roles in lysosomal biogenesis or functions, the authors found that vacuolar H^+–adenosine triphosphatase (v-ATPase), which pumps protons into lysosomes, is essential for TOR activation in response to amino acids. These observations were confirmed in cultured human cells by either chemical inhibition of the v-ATPase or reduced expression of the pump.

Earlier work revealed that amino acid–mediated activation of mTORC1 depends on the correct nucleotide loading of a heterodimeric guanosine triphosphatase (GTPase) complex of the Rag family (RagA/B and RagC/D) (*10*, *11*), which localizes to the lysosome by interaction with a Rag regulator (Ragulator) complex (*9*). Upon correct nucleotide loading and activation, the Rag complex can pull the cytosolic mTORC1 component Raptor from the cytosol to the lysosome membrane (see the figure). Rheb is localized exclusively to intracellular membranes and is therefore physically separated from cytosolic mTORC1 in the absence of amino acids. Zoncu *et al.* show that mTORC1 fails to accumulate at lysosomes after amino acid stimulation in the absence of an active v-ATPase, which suggests that the pump is part of the amino acid–driven sensory mechanism that targets mTORC1 to the lysosome in proximity to Rheb.

The v-ATPase is a multisubunit proton pump composed of one unit responsible for ATP hydrolysis (V1 sector) and one membrane domain that rotates upon ATP hydrolysis (V0) allowing protons to enter the lysosomal lumen and thereby acidify it. Semiquantitative mass spectrometry analyses and precipitation assays using recombinant proteins led to the hypothesis that Ragulator functions as a bridge linking the v-ATPase and the Rag GTPases together at the lysosome. Zoncu *et al.* further noted that amino acid stimulation and starvation reduces and strengthens, respectively, the interaction between Ragulator and the V1 but not the V0 sector. This suggests that amino acids control the interaction between Ragulator and the v-ATPase.



Amino acid sensing. (**A**) At low amino acid concentrations within the lysosome, Ragulator interacts with the v-ATPase and nucleotide loading of the Rag complex is incompatible with mTORC1 recruitment. (**B**) When amino acids are abundant, v-ATPase undergoes a structural rearrangement that alters the interaction surface between the v-ATPase and Ragulator. This changes the nucleotide loading of the Rag complex and results in recruitment of mTORC1. Rheb (in the lysosome membrane) activates mTORC1, which then phosphorylates growth-promoting targets such as S6 kinase 1.

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