New research furthers understanding of the electronic structure of graphite

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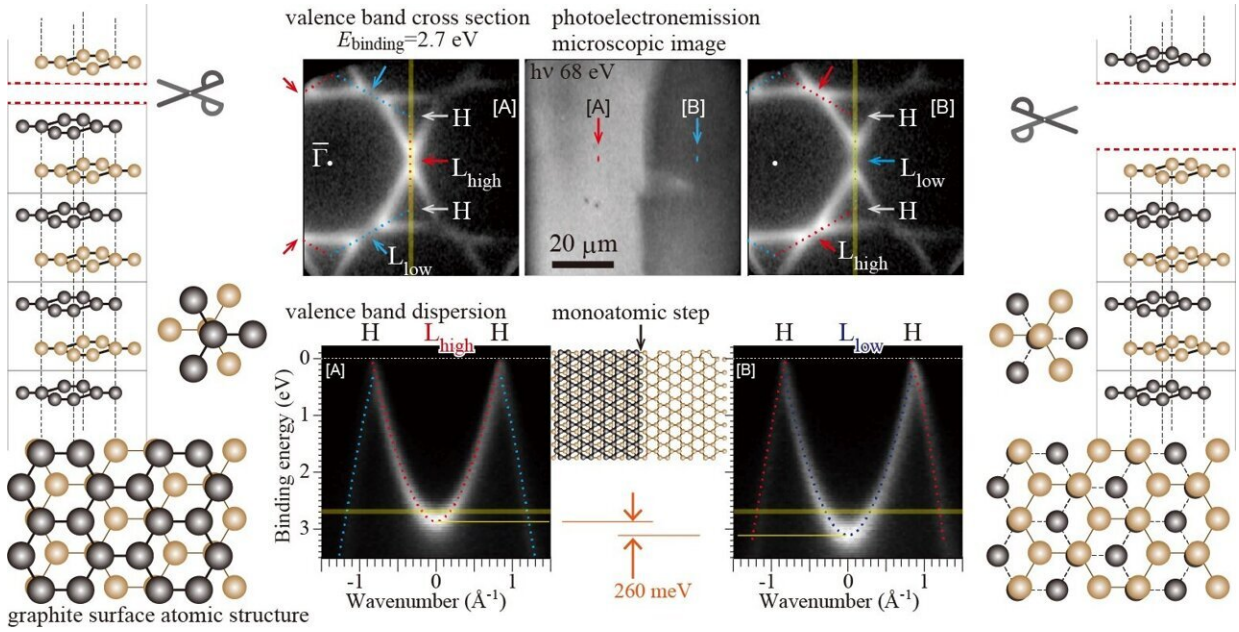

Graphite surface microscopic image and valence band structure together with atomic structure models. Credit: Fumihiko Matsui, Institute for Molecular Science in Okazaki, Japan

Graphite is an incredibly important, versatile mineral, with uses spanning industries. Because graphite can easily conduct electricity and withstand high temperatures, it is especially important for electronics. Graphite is an essential component of many batteries, including lithium-ion batteries, and demand is only increasing as new technology is developed.

For example, solar power and electronic vehicles will require increased production of the batteries and the need for graphite. Even though graphite has been thoroughly researched for decades, there is still more for researchers to uncover. Surprisingly, no spectroscopic studies have so far accurately measured the electronic states of the surface and the edge of graphite from a microscopic point of view. This is important because the improvement in battery performance depends largely on the control of the characteristics of the graphite at the tip.

In a paper published in *Physical Review B*, researchers have detailed new observations of the surface state of graphite using a newly developed photoelectron spectroscopy machine combined with electron microscope .

"In this study, we report the microscopic observation of three-fold symmetric graphite surface states coupled with bulk k_z dispersed π bands. The finding highlights the relevance of considering surface effects in bulk intrinsic electronic state measurements," said Fumihiko Matsui, a professor at Institute for Molecular Science in Okazaki, Japan. "The question we address is: how accurate can we measure the intrinsic bulk k_z dispersion?"

Crystalline structures like graphite have energy bands in what is known as a band structure. In addition to the inherent bulk band structure, there is a special electronic structure on the surface of the material, which is called the surface state. Macroscopic measurements tend to average and unrecognize the various fine structures on the surface. In the worst case, this conventional measurement technique can lead to ignoring surface states and misinterpretation of bulk-specific electronic properties. Using technique called photoelectron momentum-resolved spectro-microscopy, researchers looked at the electronic structures of graphite surface. They were able to see how the surface states interacted with the bulk bands and succeeded in imaging single-atom height steps on a graphite surface.

Understanding both surface state and band structures of graphite can help researchers understand its electrical properties as well.

Graphite is a crystalline form of carbon that is made up of many layers. Each individual layer of graphite, called graphene, is structured in a hexagonal honeycomb. The way these layers stack on top of each other affects the type of electronic band structures that are found in the graphite. "Graphite crystals with an ABAB-type stacking structure are six-fold symmetric around the z axis, whereas a surface with one type of termination is three-fold symmetric," said Matsui. When researchers looked at the dispersion of the k_z band at micrometer-scale, they found that the combination of this six-fold structure and the three-fold structure eliminated degeneracy of the π band and the symmetry was reduced.

"In this study, we have succeeded in characterizing the effect of such a coupling in a surface geometry with broken symmetry," said Matsui. "The observed bulk dispersion differs from the discrete electronic states of several layers of graphene, meaning that the measurement is also sensitive to the bulk electronic states from much deeper than the mean free path length of the emitted electrons. Moreover, the k_z dispersion bandwidth is affected by the coupling with the surface electronic state, as shown in this study. The accuracy and resolution of $k_z$dispersion bandwidth determination are limited by the electron attenuation length, especially when the surface resonance state couples with the bulk k_z-dispersed band."

Looking ahead, more theoretical research is needed to understand how these different structures work together. "Further theoretical studies of valence photoelectron emission with precise consideration of the surface effect are desired in order to clarify the k_z intensity dependence," said Matsui.

More information: Fumihiko Matsui et al, Coupling of kz -dispersing π bands with surface localized states in graphite, *Physical Review B* (2022). DOI: 10.1103/PhysRevB.105.235126