High-capacity battery, Energy materials, Nano-device

Developing the intercalation chemistry of alkali metals and molybdenum chloride in bilayer graphene system and its applications to the energy storage materials

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Abstract

The nanospace of the van der Waals (vdW) gap between structural units of two-dimensional (2D) materials offers a unique platform for growing novel 2D systems via intercalation, particularly for alkali metals and metal chlorides in bilayer graphene (BLG). This study utilized low-voltage scanning transmission electron microscopy (LV-STEM) to visualize the atomic structures of intercalated alkali metals—potassium, rubidium, and cesium—as well as molybdenum chloride in BLG. We found that intercalated AMs form bilayer structures with hcp stacking and a $C_6M_2C_6$ composition. Meanwhile, when using molybdenum pentachloride ($MoCl_5$) as an intercalant, the predominant structures were $MoCl_3$ networks, $MoCl_2$ chains, and Mo_5Cl_{10} rings, exhibiting significant lattice distortions and frequent structural transitions, which have never been observed in metal chloride systems. These findings enhance our understanding of intercalation chemistry and underscore the importance of atomic-resolution imaging in studying unique properties of these materials.

Background & Results

Alkali metals (AMs), including lithium (Li), sodium (Na), potassium (K), rubidium (Rb), and cesium (Cs), are of particular interest due to their low electronegativity, high reactivity, catalytic properties, and charge storage capability in graphite. Additionally, molybdenum pentachloride ($MoCl_5$) graphite intercalation compounds (GICs) stand out among various transition metal chloride intercalation compounds due to their high chemical stability and electronic conductivity. However, the microstructures and electronic states of AMs and $MoCl_5$ in graphite remain underexplored. This study employs bilayer graphene (BLG) as a substrate to investigate the intercalation structures of AMs, specifically K, Rb, and Cs, whose larger atomic sizes enhance STEM detection. We observed stable bilayer AM structures in BLG, while single-layer AM structures were too mobile under electron beam irradiation for clear imaging. This suggests that AM storage capacity could be improved by intercalating into graphite layers with lower crystallinity. Additionally, we found that using $MoCl_5$ powder without extra chlorine leads to a transformation into $MoCl_3$ for intercalation into the van der Waals gap of BLG. DFT analysis indicates that quantum mechanical effects similar to Peierls-type distortion may occur in $MoCl_x$ systems at low temperatures, resulting in lattice deformation and configuration changes. These findings highlight the unique quantum properties of $MoCl_x$ in confined spaces and suggest avenues for further study.

Significance of the research and Future perspective

Encapsulating novel 2D materials in BLG provides unique opportunities to tailor system properties for specific applications, such as photonics, quantum information, and energy storage. Analyzing the fine structure of 2D intercalation at the atomic scale will offer scientific insights, design strategies, and fabrication techniques for potential applications of BLG intercalation compounds.

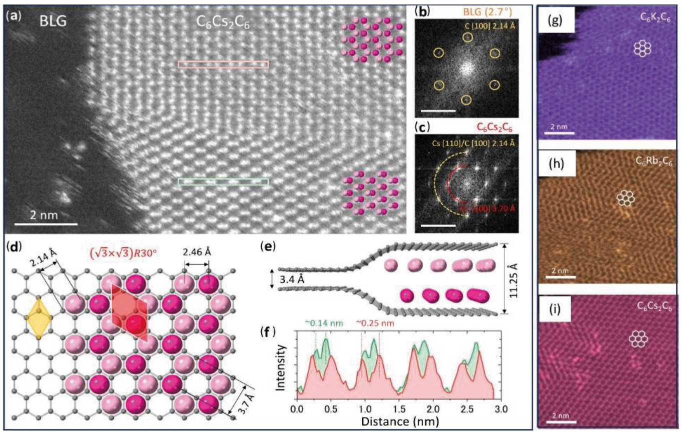

Figure 1: Scanning transmission electron microscopy (STEM) images and atomic structure of Cs, Rb and K bilayer in bilayer graphene (BLG) (C6Cs2C6).

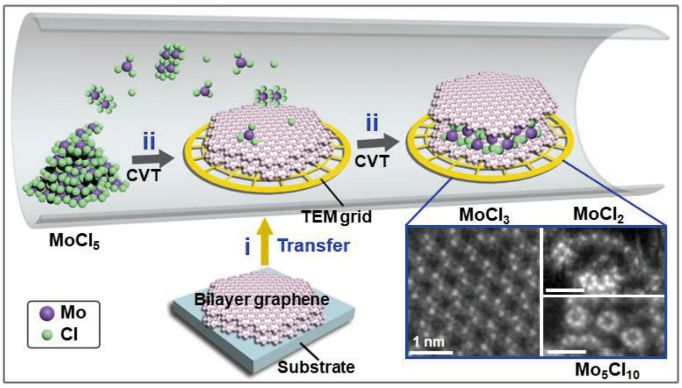

Figure 2: Molybdenum chlorides intercalation into BLG. The right bottom is STEM images of $MoCl_x$ intercalation in BLG, which show intercalated $MoCl_3$, Mo_5Cl_{10}, and $MoCl_2$ chain structures.

Patent

Treatise
Liu, Qiunan; Lin, Yung-Chang; Suenaga, Kazu et al. Molybdenum chloride nanostructures with giant lattice distortions intercalated into bilayer graphene. ACS Nano. 2023, 17(23), 23659-23670. doi: 10.1021/acsnano.3c06958
Lin, Yung-Chang; Liu, Qiunan; Suenaga, Kazu et al. Alkali metal bilayer intercalation in graphene. Nature Communications. 2024, 15, 425. doi:10.1038/s41467-023-44602-3

URL

Keyword graphite intercalation, low-dimensional materials, nanostructure characterization