

Chemistry of graphene analogues - silicene and germanene

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The research in the field of monoelemental two-dimensional materials is dominated by graphene for almost two decades. Beyond graphene is the family of unexplored heavier tetrel analogues like silicene and germanene. Compare to graphene, these materials are non-zero bandgap semiconductors and its electronic structure can be further controlled by chemical functionalization. This opens a large area of potential applications in electronic and opto-electronic as well as photocatalysis and energy storage. The layered analogues of carbon can be synthesized by both, "top-down" and "bottom-up" approach. Compare to carbon, the layered structure of silicon and germanium is metastable and have to be prepared by chemical exfoliation of suitable template. Compare to graphene, the chemistry of its heavier counterparts remains significantly less explored.[1]

The main route for top-down methods of synthesis are based on exfoliation and functionalization of Zintl phases with general formula AB_2 consisting from hexagonally arranged Si/Ge layers separated by alkaline earth atoms, typically calcium. The structure of layered Zintl phase is shown on Figure 1. The exfoliation procedure is typically based on reaction with acid at low temperature forming hydrogen terminated surface. In this contribution will be demonstrated novel methods and strategies in synthesis and functionalization of silicene and germanene monolayers. The methods providing controlled functionalization surfaces are based on formation of negatively charged silicene / germanene and subsequent reactions with halogen derivatives, formation of reactive halogenated intermediates or direct reactions of Zintl phases with bromine or iodine derivatives. The developed methods were used for introduction of various alkyl and aryl derivatives in order to control transport and optical properties of functionalized materials. The functionalized germanium derivatives exhibit strong photoluminescence, which maxima can be tuned by substitution with various alkyl and aryl derivatives. For newly developed materials were utilized various applications including gas sensors, hybrid organic-inorganic OLED devices and photocatalytic water splitting.

References

[1] T. Hartman, Z. Sofer, ACS Nano, 13 (2019) 8566-8576

Figures

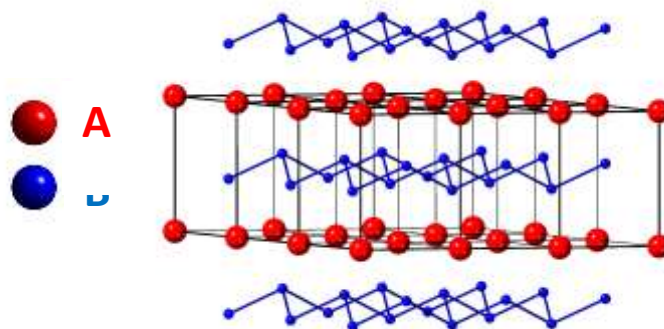


Figure 1: The structure of layered Zintl phase, where element A corresponds to silicon or germanium and element B to calcium.