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Construction of mesoscale two-dimensional honeycomb structures: a route from self-assembly building blocks to highly-organized superstructures

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Scientists have devoted great efforts to the construction of nanomaterials with well-ordered superstructures due to their potential applications in various fields, including bioengineering, semiconductors and micro-devices. The self-assembly of various building blocks is a versatile technique for generating the highly-organized superstructures. Recently, the self-assembly of colloids or nanoparticles has become a development frontier of self-assembly, which can lead to superstructures with complexity and functionalities superior to those in the molecular self-assembly [1].

Among the multifarious nanomaterials, the two-dimensional (2D) materials are a unique kind that has attracted intense interest. Especially, Graphene and transition metal dichalcogenides are distinct from other 2D materials, since their honeycomb structure endows them with extraordinary physical properties. In the molecular scale, the monolayer 2D honeycomb superlattice that resembles the graphene has been prepared. Nonetheless, construction of a mesoscale 2D honeycomb superstructures via self-assembly of colloids remains a great challenge. To date, very few related examples have been reported.

Since the self-assembly of colloids is a complicated physical-chemical process, it is difficult to reveal the related mechanism relying solely on experimental techniques. Theoretical simulation can somewhat overcome the limitation as a powerful tool that provides straightforward and detailed information of the self-assembly process. The combination of experiments and simulations in the study of self-assembly of colloids can obviously stimulate the development of this research area [2]. However, only limited studies on the colloid self-assembly have drew support from the simulations.

Very recently, Wang in Nankai University, Yan in Tsinghua University and Ungar in Zhejiang Sci-Tech University and their coworkers [3] have cooperatively developed a mesoscale version of graphene-like honeycomb superstructures. The graphene-like superstructures were constructed from POM-4POSS building blocks (formed by covalently connecting two kinds of clusters, one polyoxometalate and four polyhedral oligomeric silsesquioxanes). As shown in Figure 1(a), all the five clusters in the building blocks located in a plane and arrange in a fan-shaped manner. Transmission electron microscope (TEM) image revealed that the building blocks self-assembled into a well-ordered hexagonal honeycomb in water (Figure 1(b)). Like graphene, the honeycomb monolayers were found to form bi- and tri-layers via different stacking modes. The diverse stacking modes could appear in the same system, which was an intriguing feature of this structure.

To identify the detailed molecular organization in the honeycomb superstructure as well as its formation mechanism, they performed coarse-grained (CG) molecular simulations of the self-assembly of POM-4POSS. The simulations well reproduced the experimental observations

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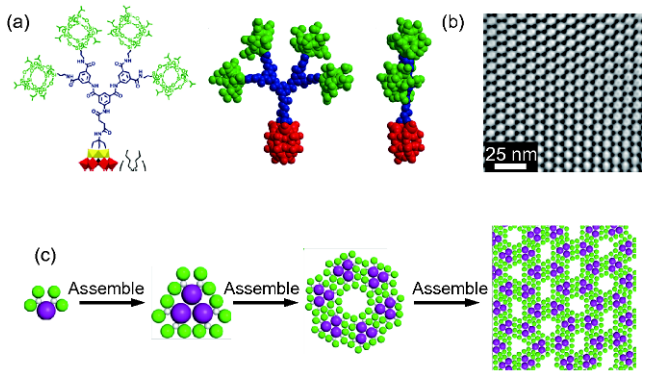

Figure 1 (a) Structure and scheme of POM-4POSS building block; (b) TEM image of the honeycomb artificial graphene formed by the POM-4POSS; (c) simulation prediction for the hierarchical self-assembly process of POM-4POSS molecule clusters into honeycomb artificial graphene (color online).

for honeycomb superstructures, which allowed the identification of the detailed molecular organization of the hexagonal honeycomb structure. Furthermore, the simulations revealed the details of hierarchical self-assembly process (Figure 1(c)): the counterion-mediated electrostatic interaction between POM blocks drives three building blocks to form a trimer. Then van der Waals interaction between POSS shells drives the trimers to form the hexagon unit cells, which finally self-assemble into the well-ordered honeycomb structures. The results indicated that the formation of triangle cluster as direct building blocks is essential for the generation of such 2D honeycomb structures. Here, the simulation not only supported the experimental work, but also addressed the challenges in studying the self-assembly mechanism.

In summary, Wang, Yan, Ungar and their coworkers have made a significant contribution to the preparation of novel 2D nanomaterials. The significance of the work is in the following three aspects: (1) The mesoscale 2D honeycomb structure was successfully constructed through the self-assembly of well-defined colloidal building blocks, which fills a blank in the self-assembly field. (2) Theoretical simulation was used as an effective tool to reveal the self-assembly mechanism, implying the crucial role of the simulation in studying the self-assembly of nanoscale building blocks. (3) A novel mechanism regarding shape-entropy driven self-assembly was proposed: the geometry of the intermediate entity formed by the elementary building blocks directly shapes the self-assembled superstructure, instead of the geometry of the elementary building block itself. The knowledge obtained from the work promises further developments of novel materials with highly-organized superstructures. In addition, the huge specific area and the porosity of the honeycomb structures can ensure highly accessible active sites and generate extremely high chemical affinity. These properties could endow the mesoscale honeycomb superstructures with a broad future of application in the fields of catalysis, sensors, electrochemistry, membranes, 2D heterojunctions, templated synthesis and complex nanoreactors.

Conflict of interest The authors declare that they have no conflict of interest.

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