Atomic visualization of structure and growth of two-dimensional clathrate hydrate

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Clathrate hydrates (CHs) are widely recognized as promising clean energy sources in nature. However, their structural understanding has largely relied on spectroscopy, leaving the microscopic mechanisms of CH nucleation and growth poorly understood. Typically, CH formation occurs under high-pressure conditions, restricting laboratory research. Here, we report the discovery of two-dimensional (2D) tetrahydrofuran (THF) hydrates on graphene/graphite surfaces, formed through vacuum deposition, serving as an ideal model system for studying hydrate nucleation and growth. Using a non-contact atomic force microscope with a CO-terminated tip, we achieved atomic imaging of hydrate structures, revealing cages composed of nine or ten water molecules encapsulating a THF molecule. These cages, connected by pentagonal and hexagonal water rings, form 2D ordered networks. By tuning the THF-to-water ratio, we identified distinct different ordered structures, demonstrating the role of THF-water interactions in shaping hydrate structures. Numerous intermediate structures were captured during hydrate formation, allowing us to reconstruct the growth process of 2D hydrates. These findings offer valuable insights into the structure and formation mechanisms of clathrate hydrates.