Bottom-Up Solution Synthesis of Graphene Nanoribbons with Tailored Widths and Edge Structures

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Abstract

Structural confinement of zero-bandgap graphene into graphene nanoribbons (GNRs) is known to induce opening of the bandgap, which can be modulated depending on their chemical structures such as the width and the edge configuration. Especially, sub-5-nm GNRs with large bandgaps and visible to near-infrared absorption are highly interesting for the nanoelectronic and optoelectronic applications. Whereas the fabrication of sub-5-nm GNRs is highly challenging by top-down methods, we have developed bottom-up approaches for making atomically precise GNRs with the width of ~1-2 nm, based on the synthetic organic chemistry. The GNR synthesis can be carried out from pre-designed monomers with two different methods, namely "in solution" through the conventional polymerization and cyclodehydrogenation reactions as well as "on surface" by annealing on metal surfaces under ultrahigh vacuum conditions.^[1,2] While the surface synthesis allows direct visualization of atomically precise GNRs by *in-situ* scanning probe microscopy, the solution synthesis has an advantage for providing large amount of GNRs for further application.^[3,4] Nevertheless, the structures of the available GNRs have been limited, hindering fine-tuning of the properties of the GNRs.

We have recently achieved syntheses of a wider variety of structurally defined GNRs with varying width and edge structures, demonstrating modulation of their optical properties.^[2] By modulating the monomer design, the width of the GNRs could be increased from ~1 nm up to ~2 nm, which accompanied the decrease of the optical bandgap from ~1.9 eV down to ~1.2 eV (Figure 1).^[3,5] GNRs 1-3 featuring different widths could all be synthesized with average lengths over 200 nm, enabling fabrication of transistor devices on single strands of GNRs (1).^[4] Furthermore, laterally extended GNR 3 displayed broad absorption over visible into the near infrared region, which allowed spectroscopic investigations over wider range of wavelengths.^[5] Further fine-tuning of the bandgap has been accomplished through modulation of the edge structure and structural motif of the GNRs, for instance by involving partial zigzag structures as well as by making GNRs with "necklace-like" structures.^[6] These results pave the way toward the application of such bottom-up synthesized sub-5-nm GNRs in next-generation optoelectronic devices.

References

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Figure 1. Structures of GNRs 1-3 with varying widths from ~1 to ~2 nm.