探針増強ラマン分光法によるグラフェンナノリボンの評価

Tip-enhanced Raman spectroscopy on chemically unzipped carbon nanoribbon

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Graphene is a graphite layer with a thickness of one atom, which shows excellent carrier mobility, transparency, mechanical strength, and flexibility. Graphene is usually a conductor without a band gap. However, when the sheet-like graphene is changed to a fine ribbon-like graphene nanoribbon (GNR), a band gap could be formed by a quantum confinement effect while keeping the physicochemical properties of graphene. GNR is thus a promising candidate for next-generation semiconductor materials. Here, we will investigate the electronic state of chemically unzipped GNR [1] using a Tip-enhanced Raman scattering(TERS).

GNRs were obtained by chemically unzipped double-walled carbon nanotubes (DWNTs) with diameters of 3–15 nm. Shortly, the DWNTs were annealed at 500 °C to induce defects and then dispersed in 1,2-dichloroethane containing poly(m-phenylenevinylene-co-2,5-dioctoxy-p-phenylenevinylene) (PmPV). The solution was sonicated for 5 h to obtain unzipped single-layered GNRs (sGNRs). Then the solution was ultracentrifuged at 50300 G for 2 h to remove any unzipped nanotubes as well as the amorphous carbon-like impurities. The supernatant was then spin-cast onto a Au(111) substrate and the substrate was annealed at 350 °C for 1.5 h to remove PmPV prior to the measurement. For TERS, silver nanowire probes were used to achieve both stable and high spatial resolution measurement[2].

From one DWNT, y-shaped two GNRs are obtained, which is derived from outer and inter nanotubes. Generally, the width of yGNR from outer nanotube is wider than that of inner nanotube. Figure (a) shows an AFM image of y-shaped GNR, which contain single layer of outer and inner GNRs. Figure (c) displays TERS spectrum obtained from yGNR. The spectrum shows the prominent peaks of GNRs, D-band (~ 1580 cm^{-1}) and G-band (~1600 cm^{-1}). TERS mapping of corresponding peaks is shown in Figure (b). The image was merged with the D-, G-band maps in magenta and blue, respectively. The TERS mapping clearly indicates that the D-band was observed only on the outer GNR, while G-band was observed on the inner GNR. From this result, we expect that first annealing process of DWNTs induce defects on the surface of outer DWNT, while less defects were induced on the surface of inner DWNTs.

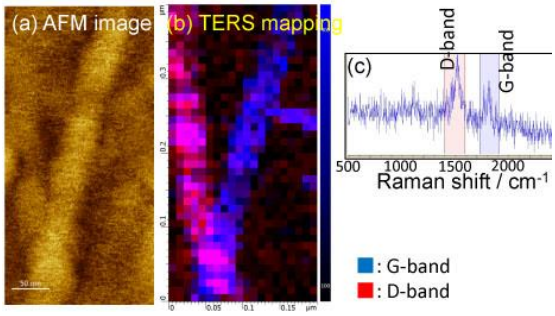

Figure. AFM image of GNR dispersed on an Au(111) substrate. (b) TERS mapping image of GNR. (c) TERS spectrum obtained on GNR.

TERS mapping of yGNR indicate that D-band was mainly observed only from GNRs from outer layer of DWNT, while GNR from inner nanotube shows mainly G-band, indicating good quality of GNR without defects. Since D-band corresponds to the chemical and physical defect of GNR, we can conclude first annealing process of DWNT induce many defects on only outer nanotubes. As such, TERS measurements allow us to reveal the reaction mechanism of unzipping process of DWNT at nanoscale. In future, chemical/physical condition of GNR will be investigated using TERS.

References

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