Supplementary Material (ESI) for Chemical Communications

Supplementary Information

DNA mediated water-dispersible graphene fabrication and gold nanoparticle-graphene hybrid

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1. Synthesis and characterization of Py-ssDNA

An amino-modified DNA (24.9 nmol, NH_2-TTTTTTGCACACGCGCAC, Bioneer corporation, Korea) was reacted with a 50-fold excess of 1-pyrenebutyric acid *N*-hydroxysuccinimide ester (Sigma Aldrich) in 120 μL Na_2CO_3/$NaHCO_3$ buffer and 66 μL of DMSO at room temperature for 5 h (Fig. S1(a)). The pyrene conjugated DNA was purified by removing unreacted 1-pyrenebutyric acid *N*-hydroxysuccinimide esters by size-exclusion chromatography on a PD-10 column. The mass of the product was determined by using matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry, in which the Py-ssDNA product (30 pmol) was mixed with 2 μL of a 3-hydroxypicolinic acid matrix solution, air-dried, and analyzed with an internal standard. Measurements were taken using a positive ion mode with 25 kV accelerating voltage, 94% grid voltage and 350 ns delay time. As shown in Fig. S1 (b), the MALDI-TOF mass spectrum of the isolated product contains a major peak at 5872 Da that matches the calculated mass (5875 Da) of Py-ssDNA.

2. Synthesis and characterization of Py-DNA/graphene hybrid

The concentration of Py-ssDNA was determined by using UV-vis spectroscopic analysis (UV-2450, SHIMADZU) based on the 260 nm absorption band. The solution was diluted with Milli-Q water to obtain the required concentration before use. Graphite flakes (0.05 mg, Sigma Aldrich) were added to a 300 μL aqueous solution of Py-ssDNA (21.3 nmol) and the mixture was sonicated in an ice-water bath (1510R-MT, BRANSONICSEM, USA) at an output power level of 70 W for 8 h. After sonication, the mixture was incubated on vortex mixer for 6 h at room temperature to increase the attachment of the Py-ssDNA molecules to the graphene surface. The resultant solution was centrifuged for 1 h at 500 rpm, and then decantation was carried out carefully by pipette removal of 250 μL of the supernatant for storage in 4 °C.

3. Synthesis of the Au NP labeled target DNA and Au NP/graphene composite

A thiol-labeled target ssDNA (18mer: 5'-SH-TTTTTTGTGCGCGTGTGC-3') was reacted with Au NP (10 nm dia.) to produce the Au NP labeled DNA according to *Nature* protocol.[1] A protecting group of HS-ssDNA (5 nmole) was removed by reacting with DTT solution in a 100 μL reaction volume for 2 h at room temperature. The deprotected HS-ssDNA was purified by size-exclusion chromatography on a PD-10 column. UV-vis spectrophotometer was employed to determine the DNA concentration based on a 260 nm absorbance. The HS-ssDNA (4 nmole) was added into a Au NP (10 pmol, 10 nm dia.) solution to make a total volume of 1.1 mL,

wrapped in a foil and placed on a vortex overnight at room temperature. A 110 μL of 0.1 M phosphate buffer (pH 7.0) was added to the Au NP solution to obtain a final phosphate concentration of 9 mM, and then incubated for 30 min. 1 M NaCl buffer was added six times for 2 days and shaken gently to reach a final concentration of 0.1 M NaCl. The final product of Au NP labeled ssDNA solution exhibited red color without aggregations. After centrifugation at 14000 rpm for 30 min, the precipitated Au NP labeled ssDNA (2 pmol) was recovered and then reacted with a 200 μL of Py-ssDNA/graphene stock solution for 6 h. Only Au NP/graphene composites were precipitated during centrifugation at 10000 rpm and then washed three times by water.

4. Instruments

TEM was performed by dropping 1 μL of a Py-DNA/graphene solution onto lacey carbon-coated grids and images were obtained by using a field emission transmission electron microscope (TECNAI F20, FEI) operated at an acceleration voltage of 200 kV. Highly magnified TEM was used to measure the number of layers by observing the edge parts. The SEM characterization of a Py-DNA/graphene is carried out by dropping 2 μL of Py-DNA/graphene solution onto a silicon wafer substrate and dried at room temperature. SEM images were recorded using a field-emission microscope (S-4800, HITACHI, Japan). An AFM image of a Py-ssDNA/graphene deposited on the silicon wafer substrate was obtained by atomic force microscope (Veeco D3100, USA) under the conditions of relative humidity of 43% at 20 ˚C with a tapping mode at a 1-3Hz scan rate and a 512×512 pixel resolution. XPS was performed on ESCA

2000 Multilab (VG Microtech) system using MgKα (hν=1253.6 Ev) with a residual gas pressure in the range of 10^{-10} Torr.

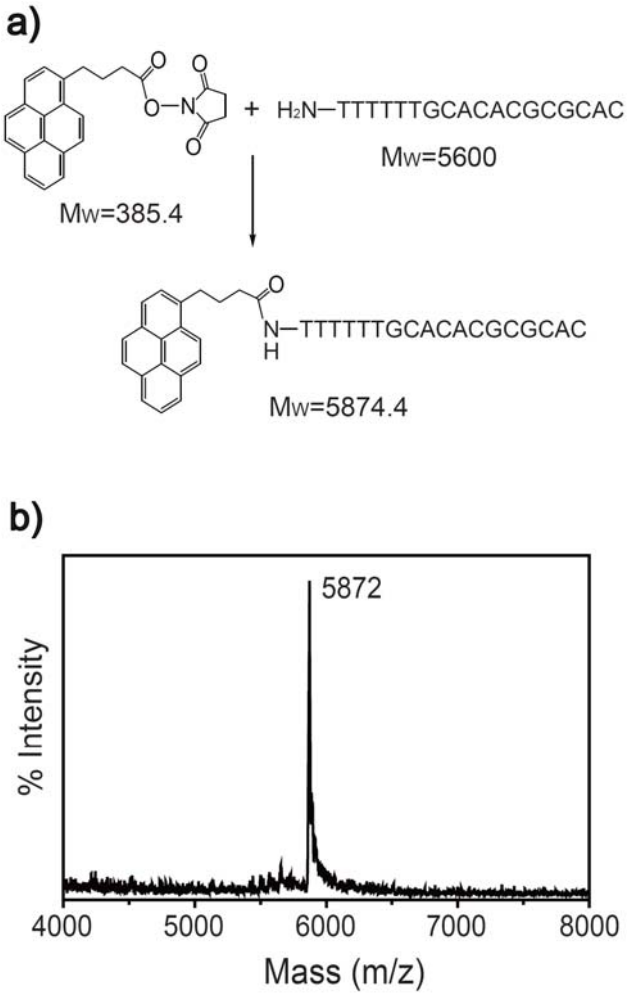

Fig. S1 (a) Synthetic scheme and (b) MALDI-TOF mass data for Py-ssDNA.

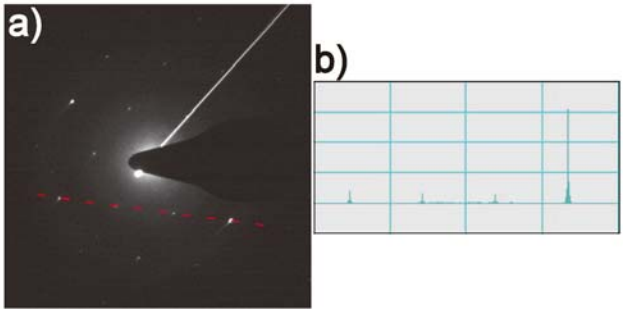

Fig. S2 (a) Electron diffraction pattern of the bi-layered graphene sheet in Fig. 2c and (b) the diffracted intensity along the red line in (a).

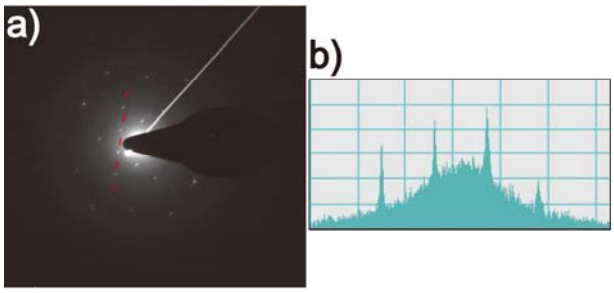

Fig. S3 (a) Electron diffraction pattern of the isolated graphene sheets in Fig. 3b after resonication of one-week incubated graphene solution and (b) the diffracted intensity along the red line in (a).

Reference

1. H. D. Hill and C. A. Mirkin, *Nature Protocols*, 2006, **1**, 324.