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Supporting Information

Creation of a Two-Dimensional Polymer and Graphene Heterostructure

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1. Materials and methods

Materials

Copper foil (0.0025mm, 99.8%) was purchased from Alfa Aesar. 300nm SiO_2 wafer was purchased from HF Kejing material technology co. LTD. Natural mica plates were purchased from The TOSAI Corporation. PMMA (Average Mw=996000, Sigma-Aldrich). Acetone (AR, Aladdin), anisole (AR, Aladdin), ethyl alcohol (99.7%, Aladdin), hydrochloric(36.5-38.0%, Sigma-Aldrich), ferric chloride (AR, Aladdin), hydrogen (Guangqi gas co. LTD), methane (Guangqi gas co. LTD), were used as received. Monomer **1** was kindly offered by Prof. A. Dieter Schlüter from ETH Zürich.

Instrumentation

Optical microscopy images were recorded by Olympus BX53M. Scanning electron microscopy (SEM) was conducted on Zeiss ULTRA 55 operated at an acceleration voltage of 10 kV. Raman spectra were acquired on confocal Raman microscopes (Renishaw inViaTM Qontor). The Raman spectrum was excited by a 532 nm laser. X-Ray photoelectron spectroscopy was carried out in ultrahigh vacuum (ca. 10^{-10} mbar) in an Omicron spectrometer with a monochromatic X-ray (AlKa)) source. Binding energies are referred to the $Cu2p_{3/2}$ at 932.2 eV. The spectra were processed with CasaXPS software (version2.3.15, Casa Software Ltd, Wilmslow, Cheshire, UK). For peak fitting, a Shirley background and symmetric Voigt functions were used. Rapid Thermal Processor AS-One 100 equipped with a 30 kW IR lamp was used to heat samples. It was operated at a 20 °C/s heating rate in forming gas.

2. Experimental Procedures

Synthesis of CVD graphene and 2DP1

CVD graphene was synthesized according to literature reported procedures [1-3]. Briefly, graphene was chemically deposited with methane as the carbon source and copper foil as the substrate. It was prepared by vacuum evaporation. The copper foil was cleaned with acetone, anhydrous ethanol and deionized water. The cleaned copper foil was loaded with corundum boat and placed in the constant temperature zone of the tubular furnace. Pumping air out of the tubular furnace and inputting H_2 for two times were conducted to get a rather clean hydrogen atmosphere. The heating function of the tubular furnace to reach the annealing temperature (1050 ℃) and inputting H_2 with a constant flow rate started at the same time. In order to give copper foil an annealing treatment, the temperature should be maintained for 5 min when it reached the annealing temperature. Subsequently, the temperature was adjusted to 1000 ℃ and CH_4 was fed into tubular furnace for 5 min. Then heating function of the tubular furnace was turned off. After the naturally cooling down to room temperature, the feeding H_2 was switched off and the sample was obtained.

A poly(methyl methacrylate) (PMMA) mediated transfer method was used to transfer graphene on 300 nm SiO_2/Si substrates. In this experiment, the PMMA solution (wt5%) was prepared with phenyl ether as solvent. A layer of PMMA was spun (rotation speed= 2000 rpm, time= 90s) on the copper foil grown with graphene which we've prepared, and then the copper foil was heated for 60s at 180 ℃ to get dried and solidified. $FeCl_3$ solution acidified with hydrochloric acid was prepared as copper etching solution. The resulting PMMA/Graphene/Cu was placed in $FeCl_3$ solution and the copper substrate was completely etched, this process would last for several hours. The copper etch solution was slowly absorbed by a glue-tipped dropper and diluted with deionized water. This procedure was repeated several times until the etch solution was completely replaced by deionized water. The PMMA/Graphene was picked up from deionized water with substrate of interest, and placed in a drying box. The material was dried for 5 minutes at 30℃ to ensure that the graphene film was fully integrated with the substrate. The PMMA/Graphene/substrate was immersed in acetone solution for more than 10 hours, during which acetone was replaced for 3 times. Finally, the soaked graphene film was placed in a tubular furnace and annealed at 300℃ to remove residual PMMA.

2DP1 was synthesized according to procedure in reference 4. Briefly, the synthesis process of 2DP1 is shown below: Dissolve monomer 1 in chloroform to prepare 1 mg/mL stock solution. Add a 100 mL of Millipore water into Langmuir-Blodgett trough (KSV NIMA, Finland). Inject chloroform solution of monomer 1 on the surface of the water. Compress the barrier of Langmuir-Blodgett trough after the chloroform evaporated. When the surface pressure reached 15 mN/m, a concentration of 5 mmol/L solution of $(NH_4)_2Fe(SO_4)_2$ was injected into the subphase. 2DP1 nanosheet formed on the surface of the water after two hours.

3. Supporting Figures

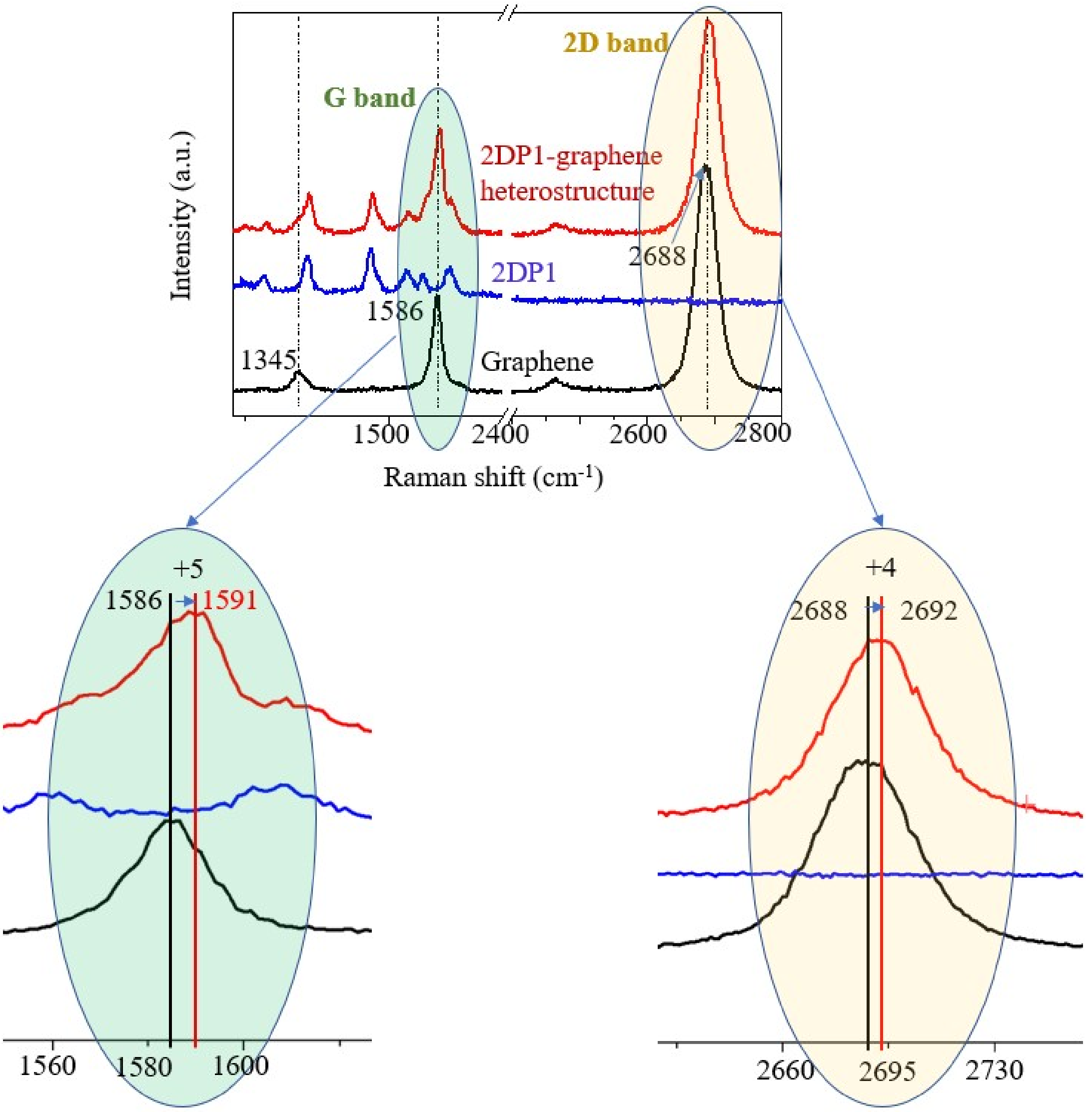

Figure S1. The partial enlarged detail of Raman shift

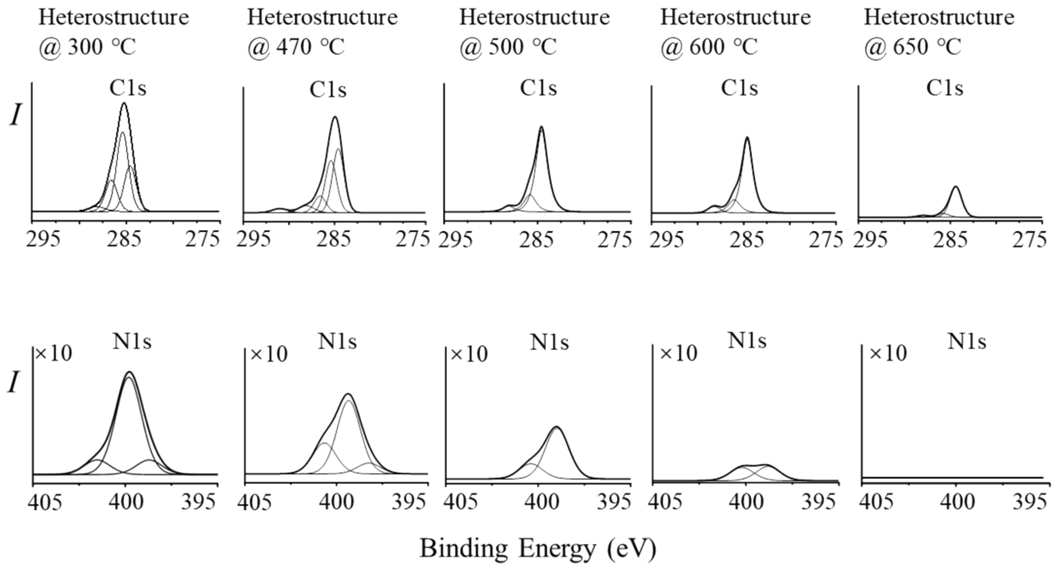

Figure S2. X-ray photoelectron spectra for 2DP1-graphene heterostructure annealed for 1 hour at different temperatures (300 ℃, 470 ℃, 500 ℃, 600 ℃, 650 ℃) on copper foil. The intensities (I) of N1s signal was amplified by a factor of 10.

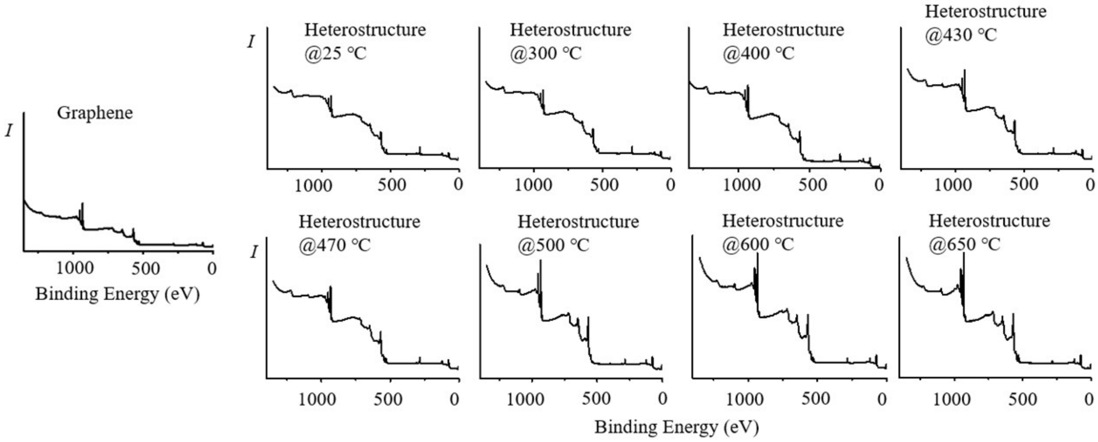

Figure S3. XPS survey of graphene, and 2DP1-graphene heterostructure before and after annealing for 1 hour at different temperatures (300 ℃, 400 ℃, 430 ℃, 470 ℃, 500 ℃, 600 ℃, 650 ℃) on copper foil.

3. References

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