

Graphene Mediated Self-Assembly of Fullerene Nanorods

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Electronic Supplementary Information (ESI)

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1. CVD synthesis of graphene:

Graphene was grown on copper substrates (25 μm thick, Alfa Aesar, 99.999% Puratronic) using chemical vapor deposition. As a first step, the copper foil was cut in to 1 cm x 1 cm pieces, and precleaned in acetic acid solution for 10 minutes, followed by an acetone and methanol rinse to remove residual organics. Next, the precleaned Cu foils were inserted in to a 1 inch quartz tube, which is heated using a horizontal split furnace. Initially, the system is pumped down to ~ 21 mTorr pressure. Once the vacuum is established, 10 sccm of hydrogen is passed through the chamber and the pressure is adjusted to 100 mTorr. The copper foils are then annealed at 1050°C in the presence of hydrogen for 30 minutes, which is followed by passing 2 sccm of methane for 15 minutes towards graphene growth. This is followed by gradually cooling the furnace to 250°C at a rate of 10°C per minute and shutting off the flow of hydrogen and methane. Simultaneously, 200 sccm of argon was introduced to purge the reactor, thereby bringing it to atmospheric pressure.

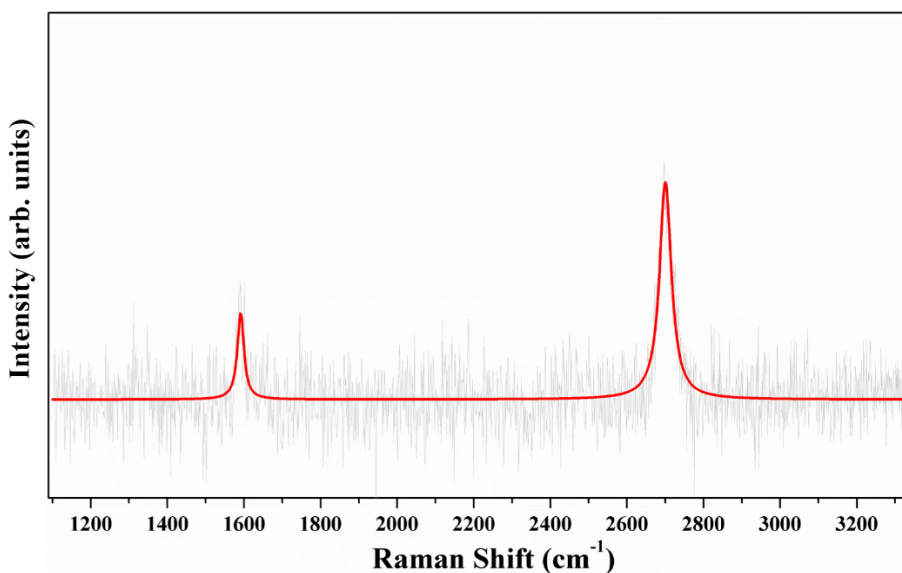


Figure S1. Raman spectra of single layer graphene grown using CVD

To confirm the growth of graphene, Raman analysis was carried out and as shown in Figure S1, characteristic G and 2D peaks were obtained, confirming the presence of predominantly single

layer graphene on copper. The Raman spectrum was appropriately corrected to account for copper background.

2. Preparation of fullerene solution:

Fullerenes are soluble in a wide range of organic solvents, including toluene (2.8 mg/ml), carbon disulfide (7.9 mg/ml) and 1,2,4-trichlorobenzene (8.5 mg/ml).¹ We use toluene to dissolve fullerenes mainly because it is the most commonly used solvent in purification and extraction of C₆₀ during processing, and is relatively safe to use. Here we prepare a solution of C₆₀ in toluene (2 mg/ml), by sonicating it in an ultra-sonication bath for 1 hour to aid complete dissolution of C₆₀.²

3. Self-assembly of fullerene structures:

Using an in-house dip-coater, the graphene/Cu (GC) foil was coated with C₆₀ by dipping it in the C₆₀/toluene solution for up to fifteen minutes. To reduce the effects arising due to surface tension, gravity and drag forces³, the dip-coated sample was carefully withdrawn by ensuring it was in a horizontal position as it was pulled, allowing for a complete surface coverage by the toluene film. The formation of fullerene self-assemblies is initiated by two drying methodologies. Horizontally aligned, uniformly sized, faceted fullerene nanorods were formed on the surface of graphene on copper by adopting a pressurized, directed air stream (2 psig) procedure that ensures complete drying of the foil.⁴ Here, the GC foil is firmly held on a flat surface and a pressurized air stream is directed over the GC foil coated with the solution, with the air nozzle directed around the copper foil at an angle of ~45 degrees. The second method involves simply allowing toluene coated on GC foil to evaporate. This leads to the formation of a variety of fullerene self-assemblies. For each case, at least 5 distinct samples were prepared and scanning electron microscopy (SEM) analysis showed that the respective DAS and SD derived

self-assemblies were very highly reproducible. Further, image analysis of 120 μm x 120 μm SEM images of DAS-derived fullerene self-assemblies obtained on graphene was carried out to ascertain the size-distribution of DAS-FNRs. Specifically, the ImageJ software was used for deriving the size-distributions, which is shown in Fig. S2. In Fig. S2, the reported sizes correspond to the FNR-length along the primary growth axis.

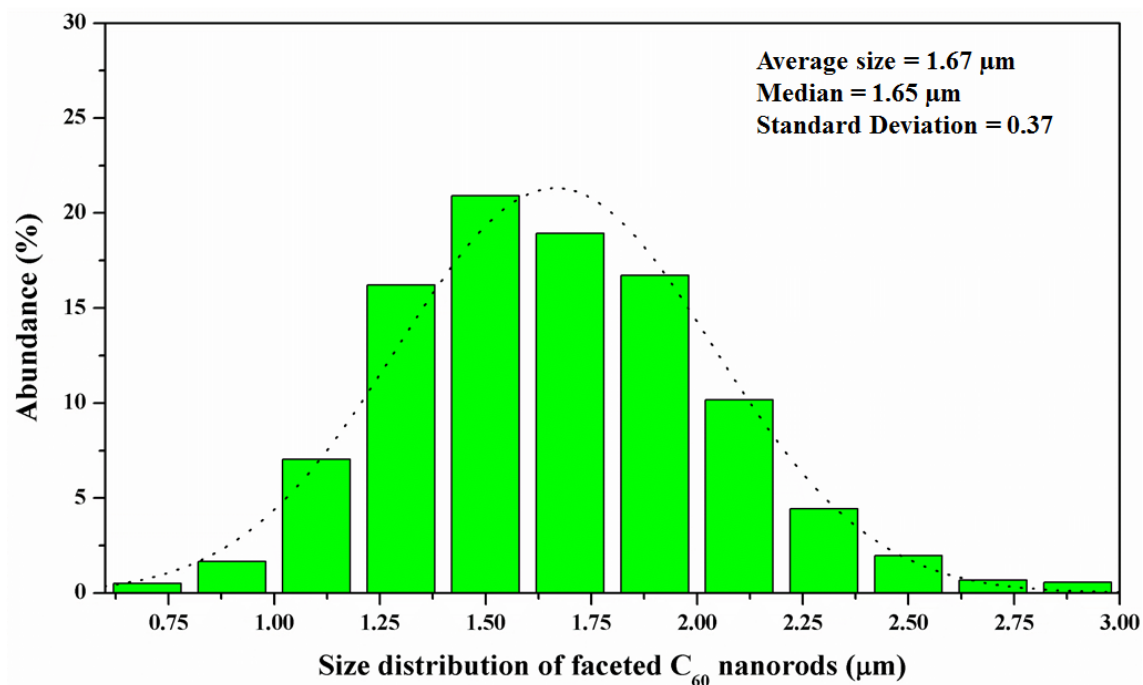


Figure S2. Size distribution of DAS-derived FNR self-assemblies on graphene.

4. Characterization of fullerene self-assemblies:

The samples were analyzed using a micro-Raman spectrometer (Jobin-Yvon Horiba Lab-Ram HR800) with an Argon ion excitation source (514.5 nm) and an average power density of 10 mW/mm^2 at a current of 20 A. The low power density was chosen to prevent/minimize photopolymerization of the fullerene nanorods. The Raman spectra were obtained at multiple spots for each sample, and were found to be similar across the samples. Furthermore, the DAS and SD dried samples were analyzed using a Philips X'PERT MPD Powder X-ray diffractometer. The angle of the receiving slit was set to 12.75° and the sample was continuously scanned. The

samples were also analyzed using a high resolution field-emission scanning electron microscopy (FE-SEM, FEI Inspec) at 2.1 nA and 10 kV and a field-emission (Hitachi S-4800 Type II) scanning electron microscope at 5 nA and 15 kV beam voltage.

5. SEM analysis of fullerene self-assemblies on copper substrates

In order to compare and contrast the role of substrates on self-assembly, SEM analysis of the SD- and DAS derived self-assembled structures on a copper substrate was carried out. The copper foils were pre-cleaned in acetic acid to remove the native oxide in addition to any possible surface contaminants. Figure S3 shows the resultant self-assemblies at different magnifications.

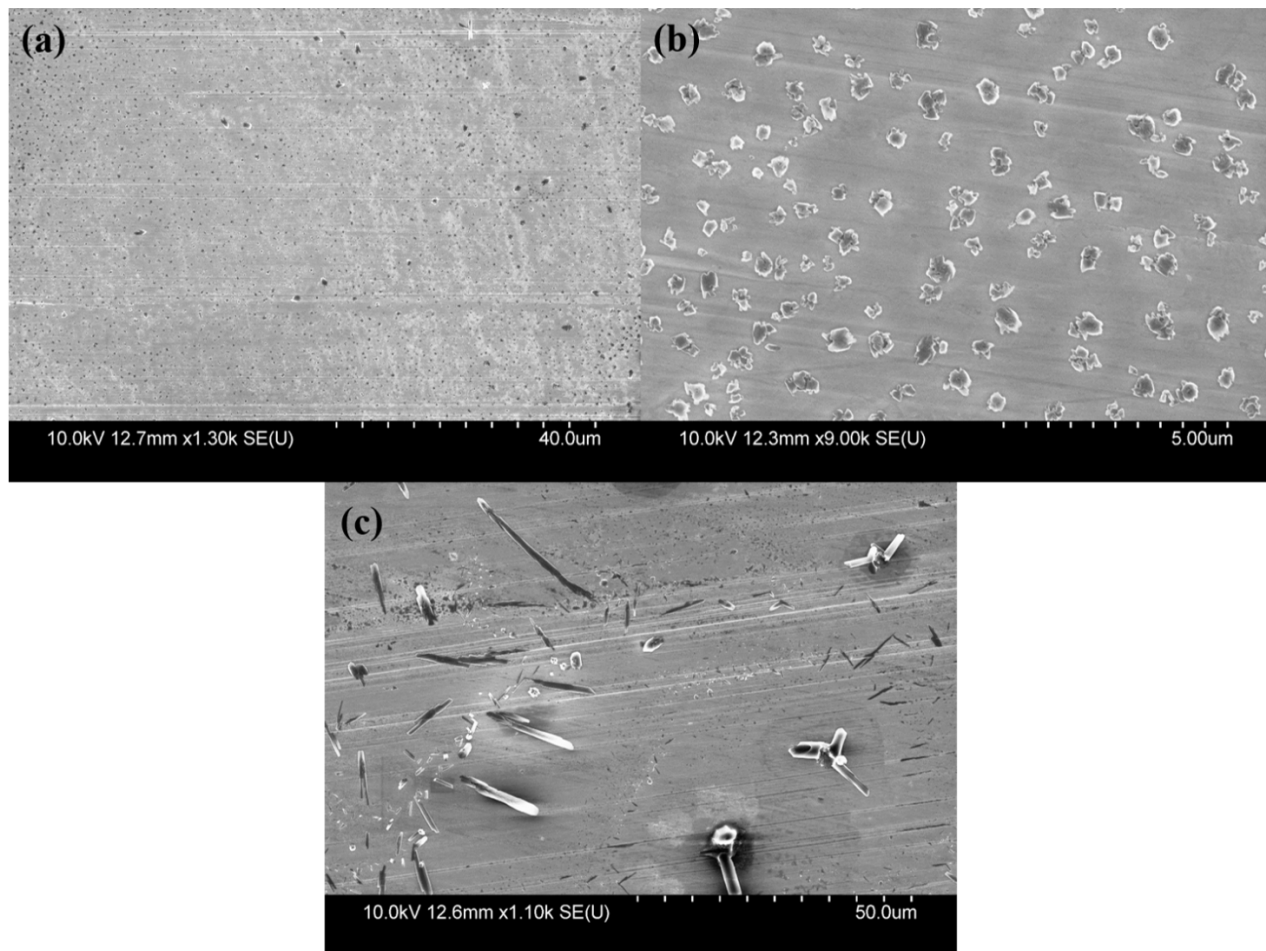


Figure S3. SEM micrographs of DAS derived self-assemblies at different magnifications: (a) scale-bar =40 μm and (b) scale bar = 5 μm and (c) SD derived self-assemblies on copper substrates (scale bar = 50 μm)

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