Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Large Scale Graphene Production by RF-cCVD Method

Enkeleda Dervishi,[*a,b] **Zhongrui Li,**[b] **Fumiya Watanabe,**[b] **Abhijit Biswas,**[c]
Yang Xu,[b] **Alexandru R. Biris,**[d] **Viney Saini,**[a,b] **and Alexandru S. Biris**[*a,b]

[a]*Applied Science Department, University of Arkansas at Little Rock, 2801 S. University Ave., Little Rock, AR 72204*
[b]*Nanotechnology Center, University of Arkansas at Little Rock, 2801 S.* University Ave., Little Rock, AR 72204
[c]*Department of Physics and Astronomy, University of Oklahoma, 440 West Brooks Street* Norman, OK 73019
[d]*National Institute for Research and Development of Isotopic and Molecular Technologies, P.O. Box 700, R-400293 Cluj-Napoca, Romania*
[*]*Corresponding Authors*

Experimental Details

The Fe-Co/MgO catalyst system with a stoichiometric composition of 2.5:2.5:95 wt.%, was prepared by the impregnation method. First, the weighted amount of metal salts, $Fe(NO_3)_3{\cdot}9H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$, were dissolved separately in ethanol with agitation. Next, MgO with a surface area of 130 m^2/g was completely dispersed into 30 ml of ethanol and the metal salt mixtures were added to this MgO solution. The final mixture was sonicated for approximately 1 hour. Next, the ethanol was evaporated under continuous agitation, and the catalyst system was further dried overnight at 60 ^{o}C. Finally, the catalyst was calcinated in air at 500 ^{o}C for 2 hours.

Few-layer graphene sheets were grown by Radio Frequency (RF) catalytic Chemical Vapor Deposition (cCVD) on the MgO supported Fe-Co bi-metallic catalyst system utilizing acetylene as a hydrocarbon source. Approximately 100 mg of the catalyst was uniformly spread into a thin layer on a graphite susceptor and placed in the center of a quartz tube with inner diameter of 1 inch. First, the tube was purged with the carrier gas (Argon) for 10 minutes at 150 ml/min. Next, the RF generator (which provides a very fast heating rate of 300-350 ^{o}C/min) was turned on to begin heating. When the temperature of the graphite boat reached 1000 ^{o}C, acetylene was introduced at 4.5 ml/min for 30 minutes. At the end of the reaction, the system cooled down under the presence of Argon for 10 minutes. The as-produced graphene sheets were purified in one easy step using diluted hydrochloric acid solution and sonication.

Characterization Techniques

Transmission Electron Microscopy (TEM) images were collected on a field emission JEM-2100F TEM (JEOL Inc.) equipped with a CCD camera. The acceleration voltage was 100 kV for the graphene analysis. The graphene nanosheets were homogeneously dispersed in 2-propanol under ultra-sonication for 30 minutes. Next, a few drops of the suspension were deposited on the TEM grid, dried, and evacuated before analysis.

The STM in this study was a homebuilt beetle-style STM with RHK technology SPM1000 controller and XMP software with Axon CV4 current amplifier. STM imaging was performed in dry N_2 at room temperature. A drop of graphene solution (flakes of graphene dispersed in iso-propanol) was deposited on the Au/mica substrate, which was then allowed to dry in air.

Atomic Force Microscopy (AFM) measurements were performed using a Veeco Dimension 3100 instrument. This instrument has a scan range of 90 μm for the "x/y" direction and 6 μm for the "z" direction, respectively. After the graphene sheets were individually dispersed into 2-propanol solution, a few drops of the final solution were pipetted on Si substrates. Next, the substrates were air dried and placed directly under the AFM tip for morphology analysis.

Brunauer-Emmett-Teller (BET) and Langmuir surface area analyses were determined by recording nitrogen adsorption/desorption isotherms at 77 K using a static volumetric technique with a Micromeritics ASAP 2020 instrument. Before the physisorption measurements, the graphene sample was degassed at 623 K for 4 h under vacuum.

Raman scattering spectra were recorded at room temperature using Horiba Jobin Yvon LabRam HR800 equipped with a CCD. A spectrometer with a grating of 600 lines/mm and a He-Ne laser (633 nm) was used as an excitation source. The laser beam intensity measured at the sample was kept at 5 mW and Raman shifts were calibrated with a silicon wafer at a peak of 521 cm^{-1}.

The X-ray powder diffraction profiles of the graphene sheets were recorded in the θ-2θ mode on the Bruker D8 Discovery diffraction system system (Bruker AXS

Corporation). The monochromatic Cu *Kα* radiation line and general area detector diffraction system were used as an excitation source and detector, respectively. The experiments were carried out in Bragg-Brentano geometry. Quantitative analysis was performed with whole pattern fitting and Rietveld refinement.

Atomic Force Microscopy

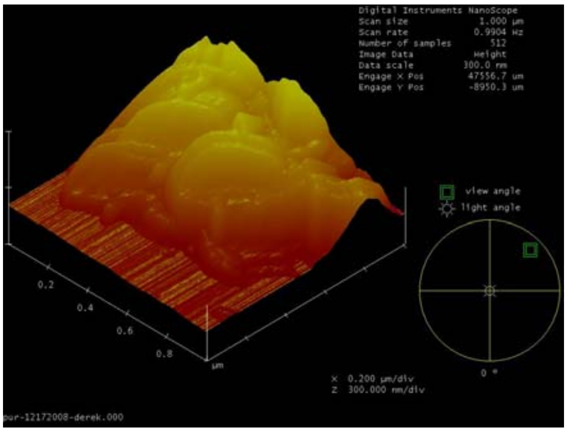

Figure S1. 3-D representation of a 1 µm × 1 µm AFM scan of graphene sheets overlaid on the Si surface.

X-ray Diffraction Analysis

The number of graphene layers was calculated by using the value of the d-spacing and the size of the crystallite. Bragg's law was used to estimate the value of the d-spacing as shown by the following formula:

$$n\lambda = 2d \cdot \sin\theta$$

where λ is the wavelength of incident x-rays (in this case 1.54 $\acute{A}$) and θ is the scattering angle of the C(002) peak.

The crystallite size was estimated from the diffraction peak widths using the Scherrer equation:

$$\beta_{hkl} = \frac{K\lambda}{L_{hkl}\cos\theta_{hkl}}$$

where β is the width of the peak at half maximum intensity of a specific phase (*hkl*) in radians, K is a constant and in this case is taken equal to 0.9, λ is the wavelength of incident x-rays, θ is the center angle of the peak and L is the crystallite length.