Title: Processing and Functionalization of Vertical Graphene Nanowalls by Pulsed Laser Irradiation

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Experimental details

VGNWs synthesis: VGNWs were deposited on commercial Papyex paper (purchased by Mersen) by inductively coupled plasma-chemical vapor deposition (ICPCVD). Briefly, the deposition reactor was an ICP-CVD system (13.56 MHz, power = 440 W) comprising a long quartz tube, a radio frequency (RF) resonator for producing remote plasma, and a tubular oven. The Papyex was cut in pieces of 3x4 cm^2. They were cleaned with isopropanol and distilled water and dried before introduced in the reactor. The sample was positioned 30 cm away from the plasma zone and heated to a temperature of 750 ◦C while reducing the reactor pressure to approximately 10^{-4} mTorr using a turbomolecular pump. Initially, the Papyex surface was cleaned by subjecting it to H_2 plasma. This cleaning process involved applying an RF power of 400 W at a pressure of 400 mTorr of H_2 for 5 min. Subsequently, the H_2 flow was halted,

and a CH_4 plasma was generated under the same RF power and pressure conditions to initiate the growth of graphene nanowalls (GNWs). The growth of VGNWs took place for a duration of 30 min. The GNWs on Papyex sample was then allowed to cool down to room temperature (approximately 20 ◦C) under vacuum. Finally, a short-duration O_2 plasma treatment was administered to the VGNWs surface to enhance its hydrophilicity. This treatment involved applying an RF power of 40 W at a pressure of 400 mTorr for 30 s. Following the completion of the process, the VGNWs on Papyex sample was remove from the reactor.

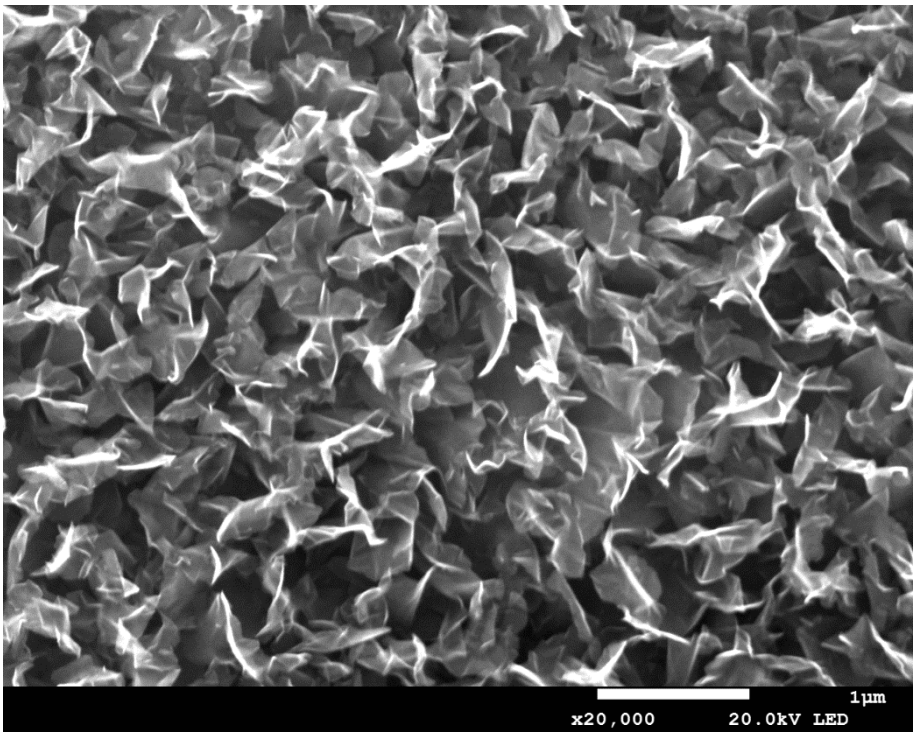
Mo deposition: The VGNWs-on-Papyex sample was loaded in a sputtering chamber, which is coupled in line with a CVD oven. A 5 mm thick circular segment cut from a graphite bar was used as a sample holder. The whole magnetron sputtering and CVD oven system is a single unit, that is, there is no separation between the sputtering chamber and quartz oven. This system facilitates the deposition of metals via magnetron sputtering and consecutive thermal annealing under vacuum without exposure to the atmosphere. The pressure of the reactor was decreased to $\sim 10^{-3}$ mTorr using a turbomolecular pump. Mo was deposited on VGNWs/ Papyex by magnetron sputtering a high-purity Mo target (99.99%) at an RF power of 100 W in an Ar pressure of 70 mTorr. The deposition rate of Mo on Papyex was ∼10 nm/ min, according to a prior calibration conducted on a glass substrate.

Laser Irradiation: Samples were positioned on a flat holder behind (at about 10 mm) the quartz window of a stainless optical chamber (500 mL internal volume), which was mounted on a computer-controlled x-y translation stage, allowing a maximum positioning resolution. The chamber was equipped with appropriate gas inlets and outlets to enable control and variability of ambient conditions. A commercial probe ((Thermovac TM20, Leybolt Hereous) was attached via a special port and used for monitoring the ambient pressure during measurements. A KrF excimer laser (LPX 200, Lambda-Physik) emitting pulses of λ=248 nm in wavelength and τ_{FWHM}=34 ns pulse duration was used as a laser source for these experiments. The laser

beam was incident, through an iris, at 0° onto the specimens at an energy density of 1.47-282 mJ cm^2. Series of 1-100 pulses at a repetition rate of 10 Hz was used. A convex lens (CL) focuses the beam onto the sample's surface.

Physical and Chemical Characterization. The morphology of the samples was studied using scanning electron microscopy (SEM) (JEOL JSM-7001F, operated at 20 kV). SEM images were treated using ImageJ software. The vibrational modes of the samples were studied using a Raman microscope (HR800, Lab-Ram; HORIBA France SAS, Palaiseau, France) with a 532 nm solid-state laser (laser power = 5 mW; diameter = ∼1 μm). All data related to Raman spectroscopy and SEM are acquired my measurements performed in the central area of the substrate and always at least 100 μm away from the substrate edges, to exlude inhomogeneities originating form variations in gas flow velocities. For X-ray diffraction (XRD) measurements, a PANalytical XPert PRO MPD Bragg−Brentano powder diffractometer with a 240 mm radius was used. Samples were irradiated with a Co Kα radiation (λ = 1.789 Å) in a 2θ range from 4 to 99° with a step size of 0.017° and measuring time of 200 s per step.

Supplementary figure 1: SEM image of pristine VGNWs prior to laser irradiation.



Supplementary figure 2: EDS spectra of the Mo particles deposited on the VGNWs nanostructure.