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From biomass wastes to large-area, high-quality, N-doped graphene: Catalyst-free carbonization of chitosan coatings on arbitrary substrates

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Experimental

Prior to coating, the quartz supports were treated to increase their surface hydrophilicity. For this purpose the quartz plates (1 x 1 cm^2, 1 mm thick) were immersed overnight in a 1 M HCl aqueous solution and then washed with Milli Q water, acetone and isopropanol by sonication for 15 min in each solvent. After cleaning, the quartz plates were submitted to ozonization during 30 min to decompose any residual organic matter. Afterwards, an aqueous solution of chitosan (0.224 g, high quality chitosan of MW 60,000-120,000 from Aldrich, ref. 740063, dissolved in a 5 ml of 0.3 M acetic acid aqueous solution) was deposited on the freshly clean quartz support by spin coating (velocity varying from 2000 to 6000 rpm). This chitosan sample contains a minimum of 93 wt% of chitosan and a maximum beta-glucan content of 5 wt%. The percentage of metal is unknown. The polysaccharide film was annealed on quartz in an oven under argon atmosphere at 200 ^{0}C for 2 h. Then, the annealed film was cooled down at room temperature and heated again up to 800 ^{0}C gradually at a 5 ^{0}C min^{-1} rate.

Textural and analytical properties measurements:

The thickness of the films was determined by an AMBIOS optical profilometer with a nanometric resolution. Transmission optical spectroscopy of the graphene layers on quartz was determined using a Cary 5G spectrophotometer. The transparency of freshly cleaned quartz plates were taken as 100 % transmittance. Raman spectra were recorded at ambient temperature with a 514 nm laser excitation on a *Renishaw In Via* Raman spectrometer equipped with a CCD detector. TEM images were recorded in a Philips CM300 FEG system with an operating voltage of 100 kV. XPS spectra were recorded on a SPECS spectrometer equipped with a Phoibos 150 9MCD detector using a non-monochromatic X-ray source (Al and Mg) operating at 200 W. The samples were evacuated in the prechamber of the spectrometer at 1 x 10^{-9} mbar. Some of the samples have been activated in situ in nitrogen flow at 450 ^{0}C for 3 h followed by evacuation at 10^{-8} mbar. The measured intensity ratios of components were obtained from the area of the corresponding peaks after nonlinear Shirley-type background subtraction and corrected by the transmission function of the spectrometer. Electrical conductivity measurements were performed using a potentiostat coupled with a four tips head or by deposition of gold. Figure 3 shows a photograph four tips set up that was contacted with the graphene film with a control pressure regulated by a micrometric nob. Deposition of gold was made in a vapour deposition chamber and subliming gold on the graphene film cover by a suitable mask.

Fig. S1. SEM image of the chitosan film before (a) and after (b) annealing at 200 ^{o}C for 2 h.

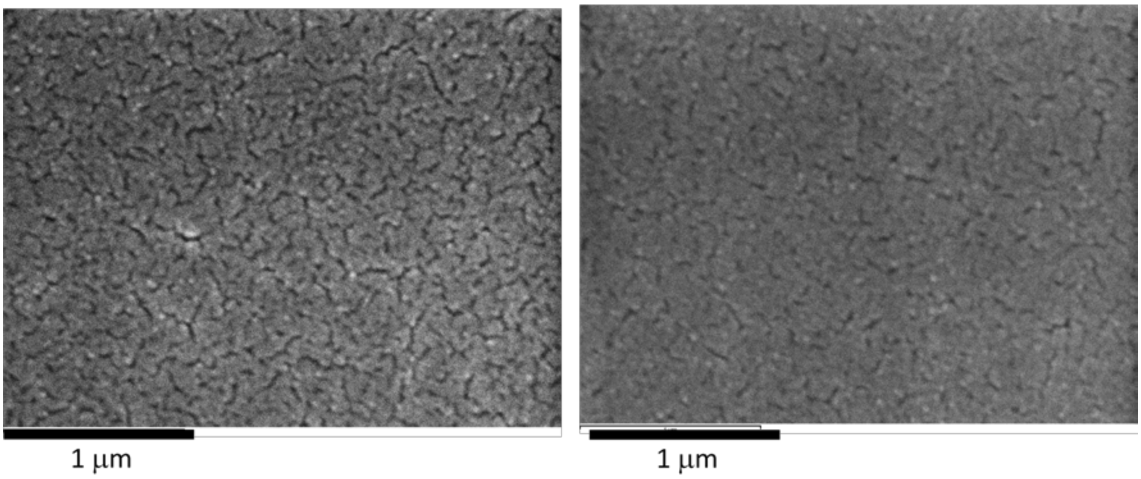
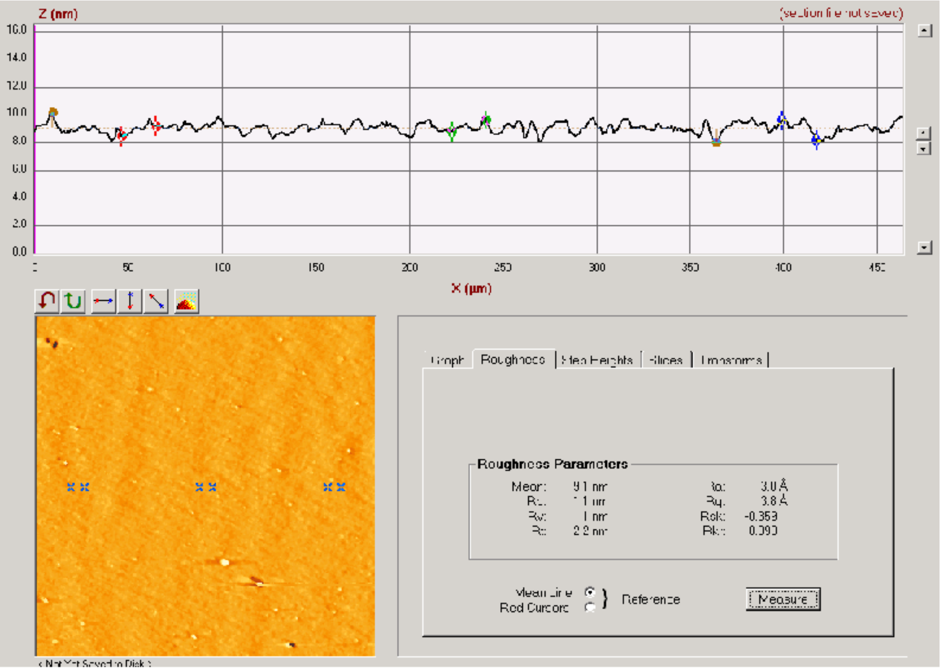


Fig. S2 View of the single-layer graphene surface obtained by profilometry (resolution higher than 1 nm). The top panel provides a view of the roughness of the surface.



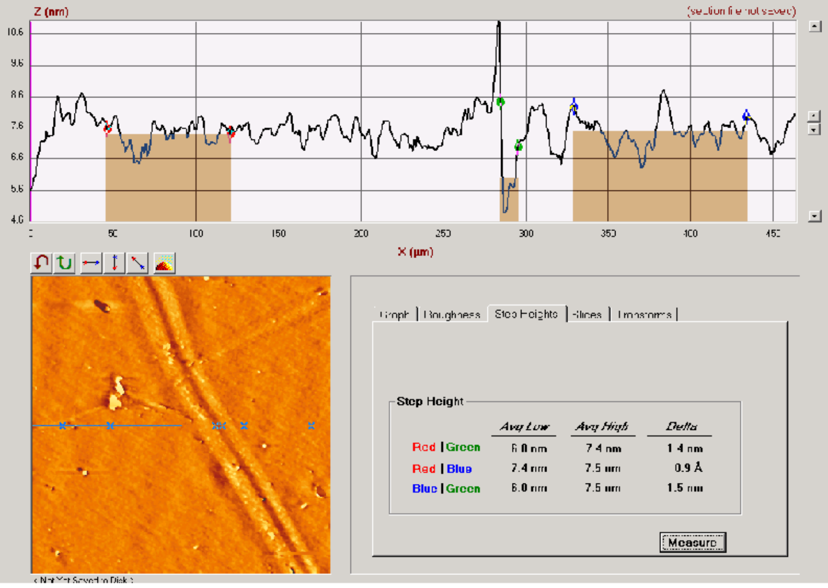
Roughness Parameters

Mean:	9.1 nm	Ra:	3.0 Å
Rp:	1.1 nm	Rq:	3.8 Å
Rv:	1 nm	Rsk:	-0.359
Rt:	2.2 nm	Rku:	0.090

Mean Line ● } Reference
Red Cursors ○

Fig. S3. Images of two-layers graphene (a) and four layers graphene (b) obtained from profilometry. The scratchs in the Figs. have been made on purpose to determine the vertical height.

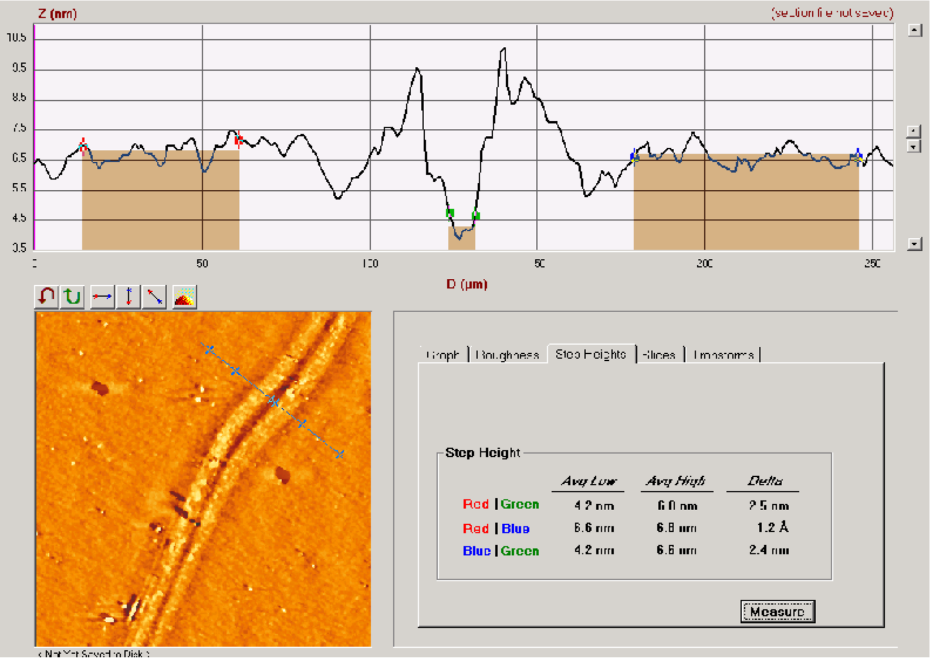
a) Note that the vertical distance between the average of the red and green or the blue and the green side is 1.4 nm.



Step Height

	Avg Low	*Avg High*	*Delta*
Red | Green	6.0 nm	7.4 nm	1.4 nm
Red | Blue	7.4 nm	7.5 nm	0.9 Å
Blue | Green	6.0 nm	7.5 nm	1.5 nm

b) Note that the vertical height in the profilometric image between the red and the green or the blue and green sides is 2.4 nm.

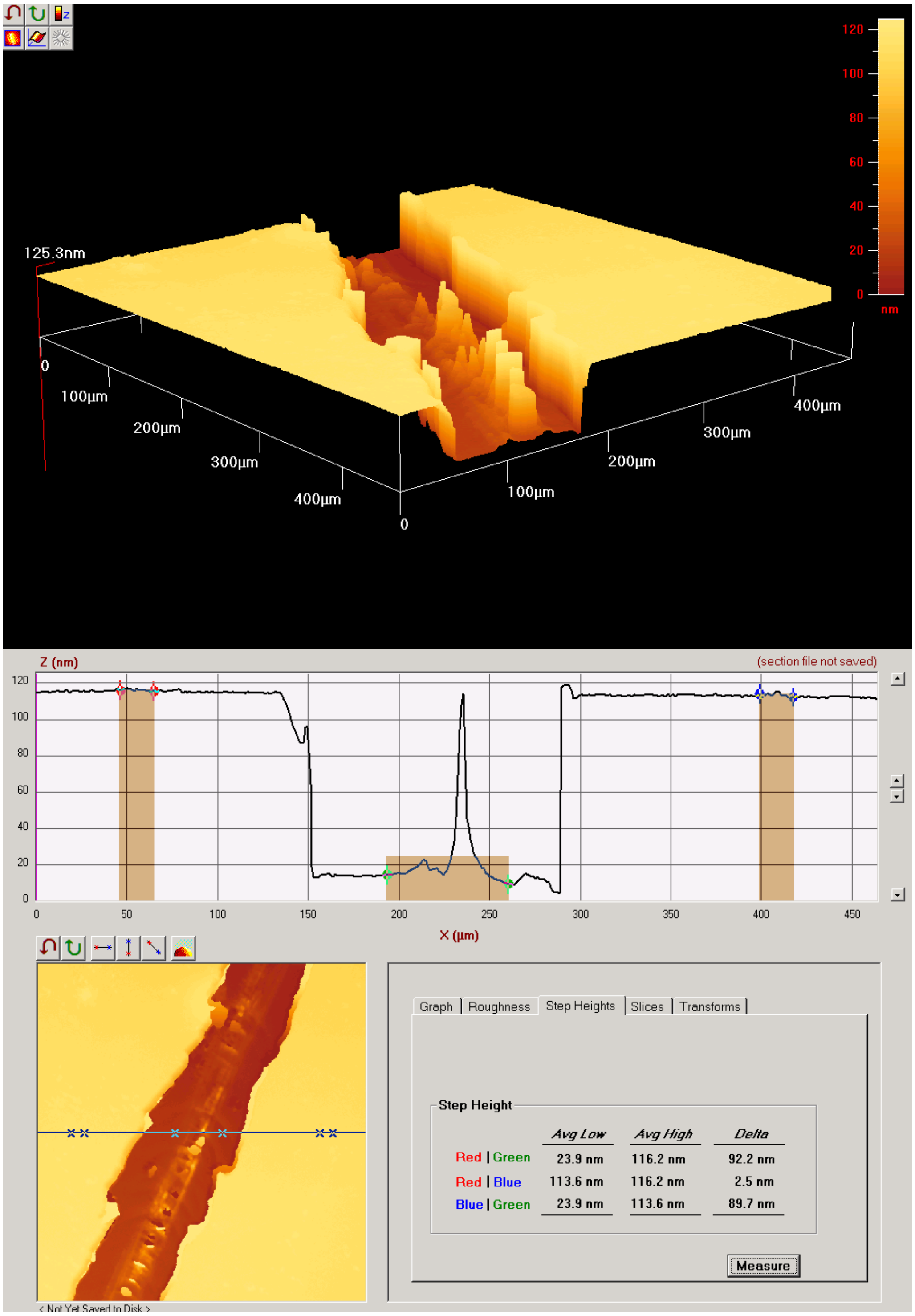


Step Height

	Avg Low	Avg High	Delta
Red | Green	4.2 nm	6.0 nm	2.5 nm
Red | Blue	6.6 nm	6.8 nm	1.2 Å
Blue | Green	4.2 nm	6.6 nm	2.4 nm

Fig. S4. Control of chitosan films thickness by varying concentration and spinning speed. All the chitosan films were obtained by dissolving 224 mg of chitosan and 90 mg of HOAc in the appropriate volume of water and spin casting on freshly clean quartz slides: a)100 nm chitosan film obtained by dissolving chitosan and HOAc in 5 ml of H_2O and spinning at 2000 rpm. After pyrolysis this film renders 20-layers graphene; b) 50 nm chitosan film obtained by dissolving chitosan and HOAc in 10 ml of H_2O and casting at 2000 rpm. After pyrolysis this film renders a 10-layers graphene sheet; c) 20 nm chitosan film spin cast at 6000 rpm the solution obtained by dissolving chitosan and HOAc in 10 ml H_2O. After pyrolysis this film renders a four-layer graphene sheet; d) 10 nm chitosan film obtained by dissolving chitosan and HOAc in 20 ml H_2O and spin cast at 6000 rpm. After pyrolysis this film is converted in two-layers graphene; e) 5 nm chitosan film obtained by dissolving chitosan and HOAc in 25 ml of H_2O and spin cast the solution at 6000 rpm. After pyrolisis this film gives a single-layer graphene film

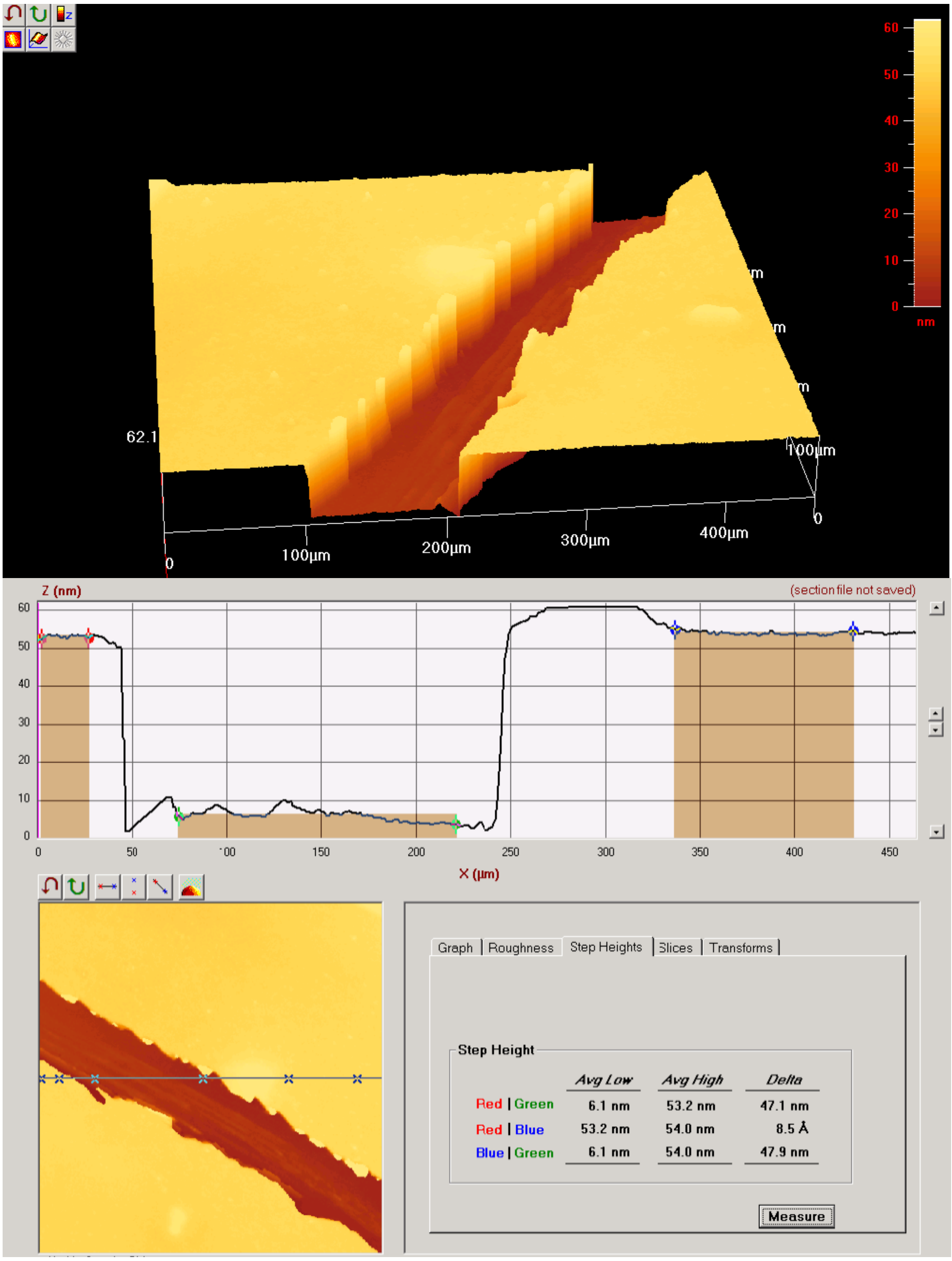
a)



Step Height

	Avg Low	Avg High	Delta
Red | Green	23.9 nm	116.2 nm	92.2 nm
Red | Blue	113.6 nm	116.2 nm	2.5 nm
Blue | Green	23.9 nm	113.6 nm	89.7 nm

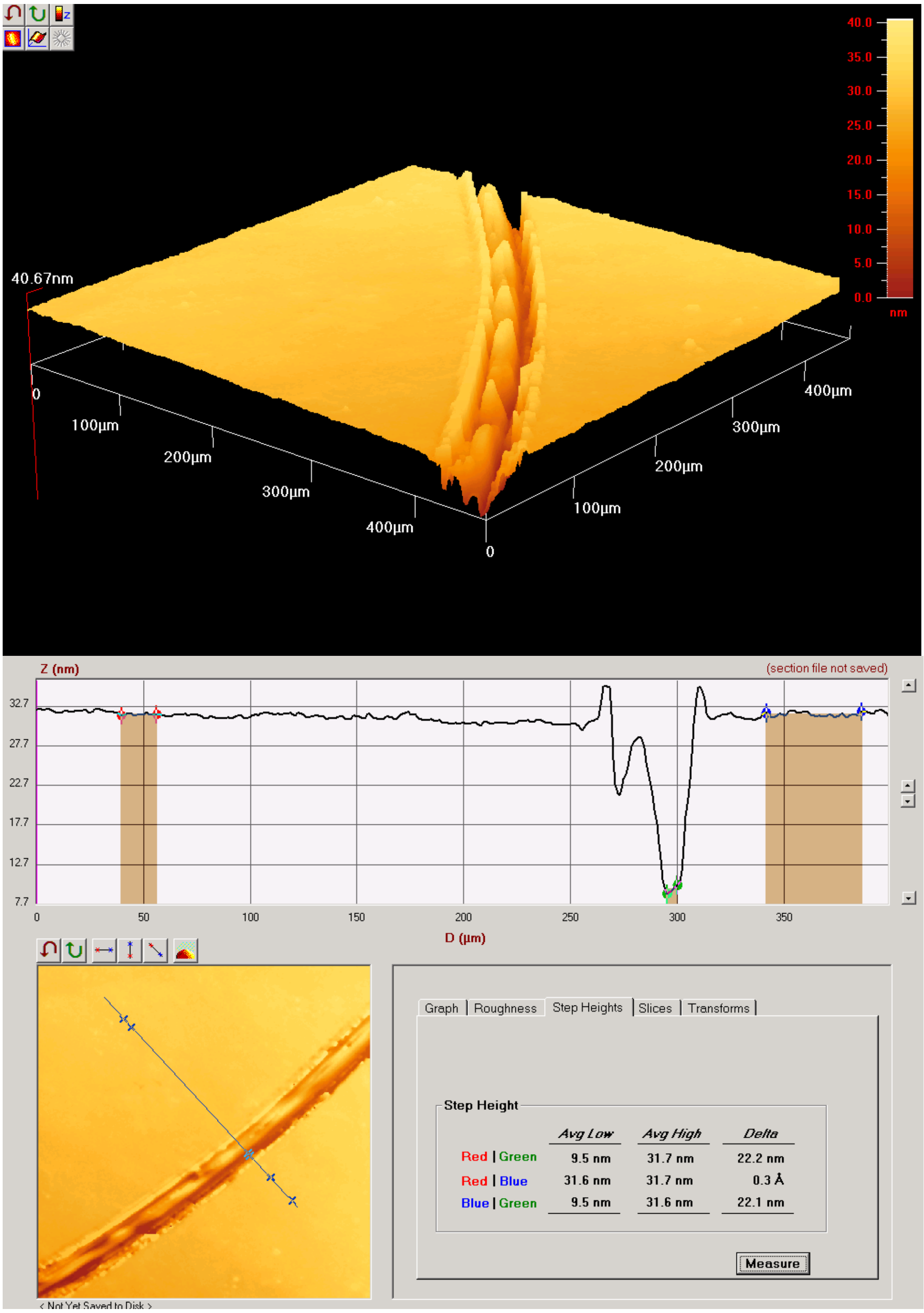
b)



Step Height

	Avg Low	Avg High	Delta
Red | Green	6.1 nm	53.2 nm	47.1 nm
Red | Blue	53.2 nm	54.0 nm	8.5 Å
Blue | Green	6.1 nm	54.0 nm	47.9 nm

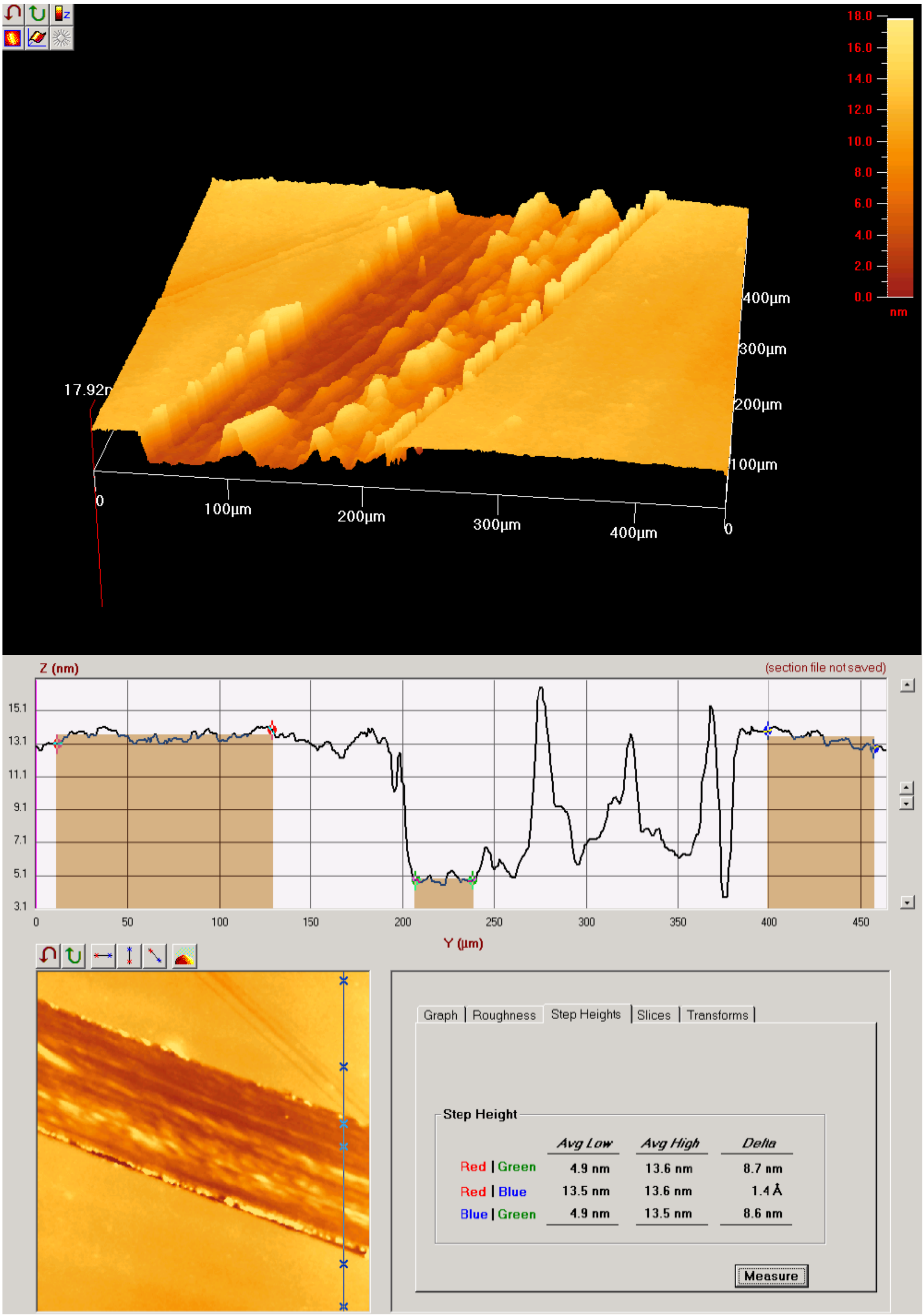
c)



Step Height

	Avg Low	*Avg High*	*Delta*
Red | Green	9.5 nm	31.7 nm	22.2 nm
Red | Blue	31.6 nm	31.7 nm	0.3 Å
Blue | Green	9.5 nm	31.6 nm	22.1 nm

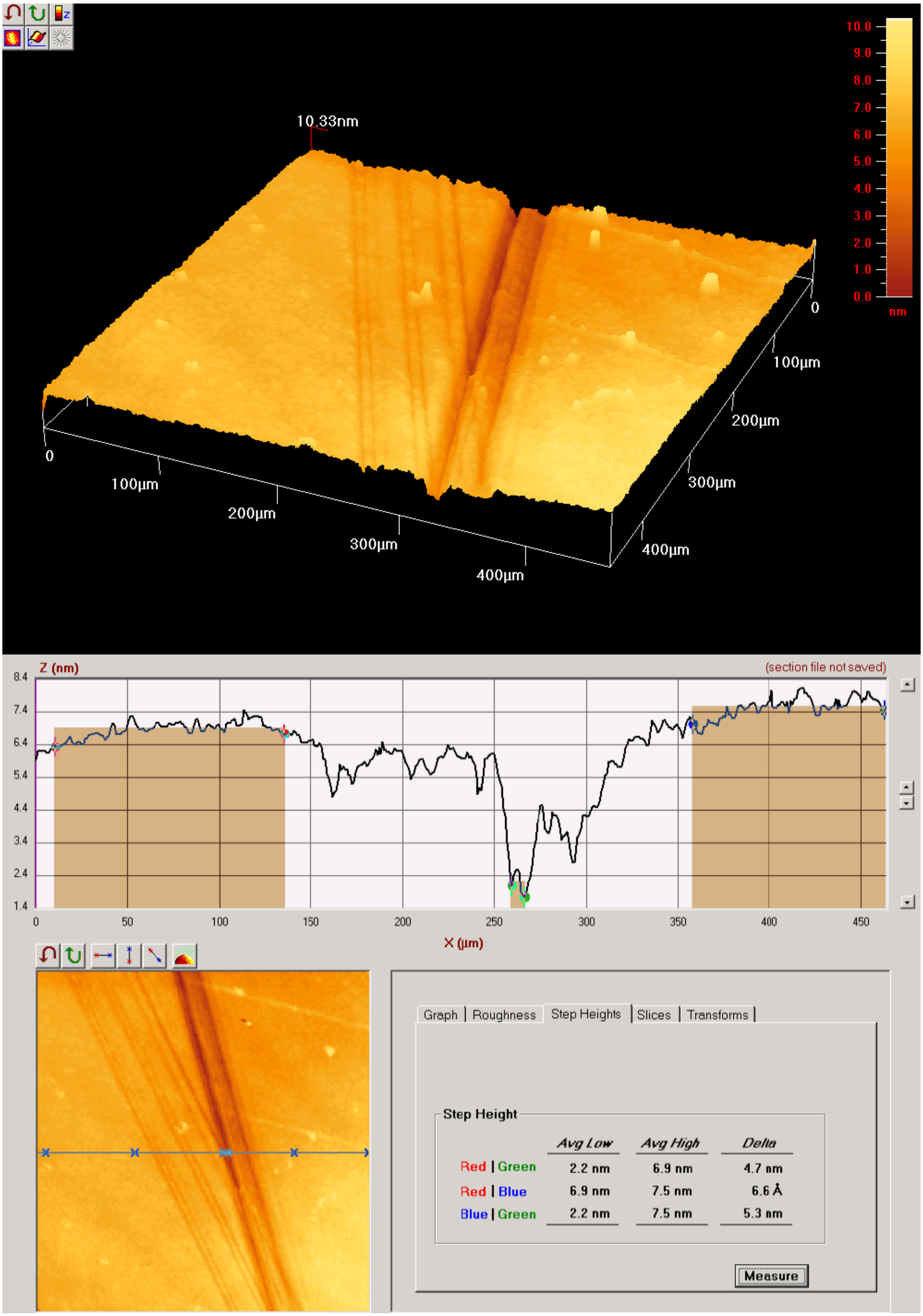
d)



Step Height

	Avg Low	Avg High	Delta
Red | Green	4.9 nm	13.6 nm	8.7 nm
Red | Blue	13.5 nm	13.6 nm	1.4 Å
Blue | Green	4.9 nm	13.5 nm	8.6 nm

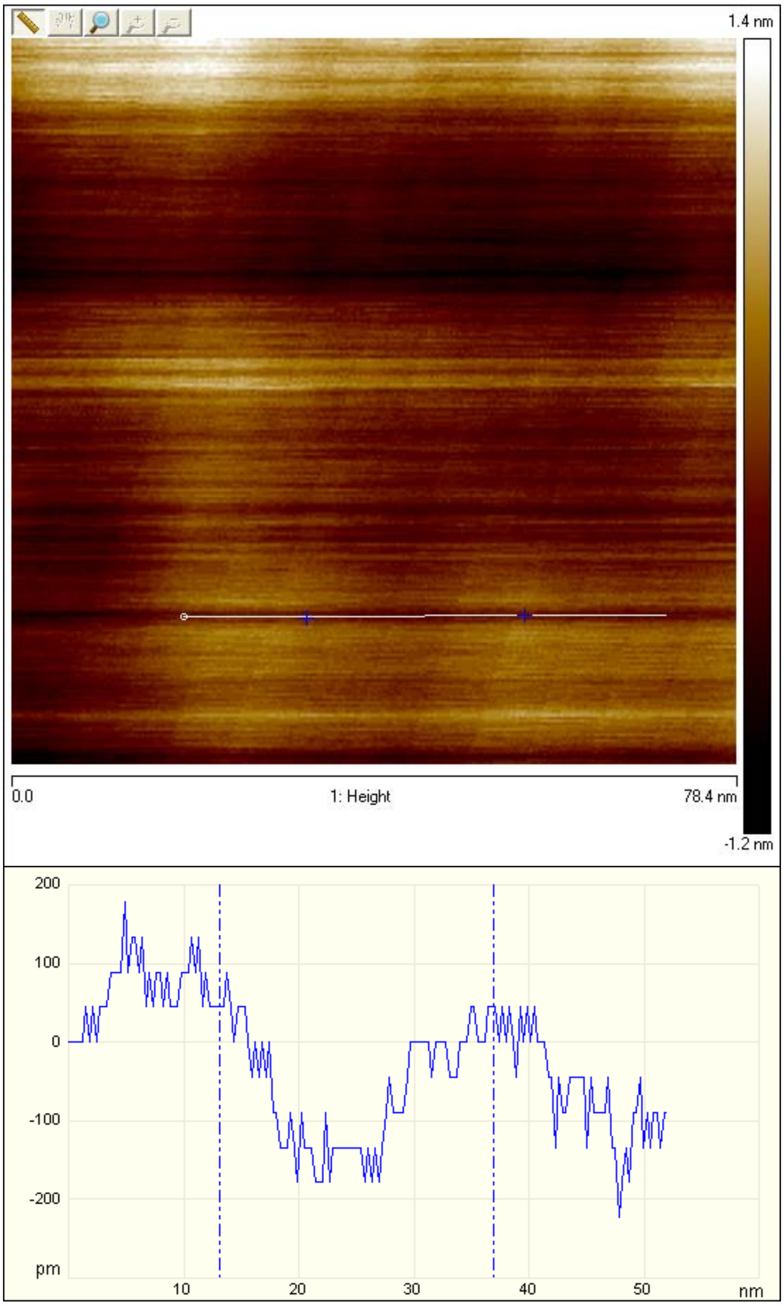
e)



Step Height

	Avg Low	Avg High	Delta
Red | Green	2.2 nm	6.9 nm	4.7 nm
Red | Blue	6.9 nm	7.5 nm	6.6 Å
Blue | Green	2.2 nm	7.5 nm	5.3 nm

Fig. S5. AFM images (in height and amplitude) of a single layer graphene sheet. In the first panel the variation in height in the maximum range of 3 nm is presented together with a white line whose vertical profile changes in 100 pm. In the second panel the same surface is presented in amplitude and the profile of the white line in mV is shown.



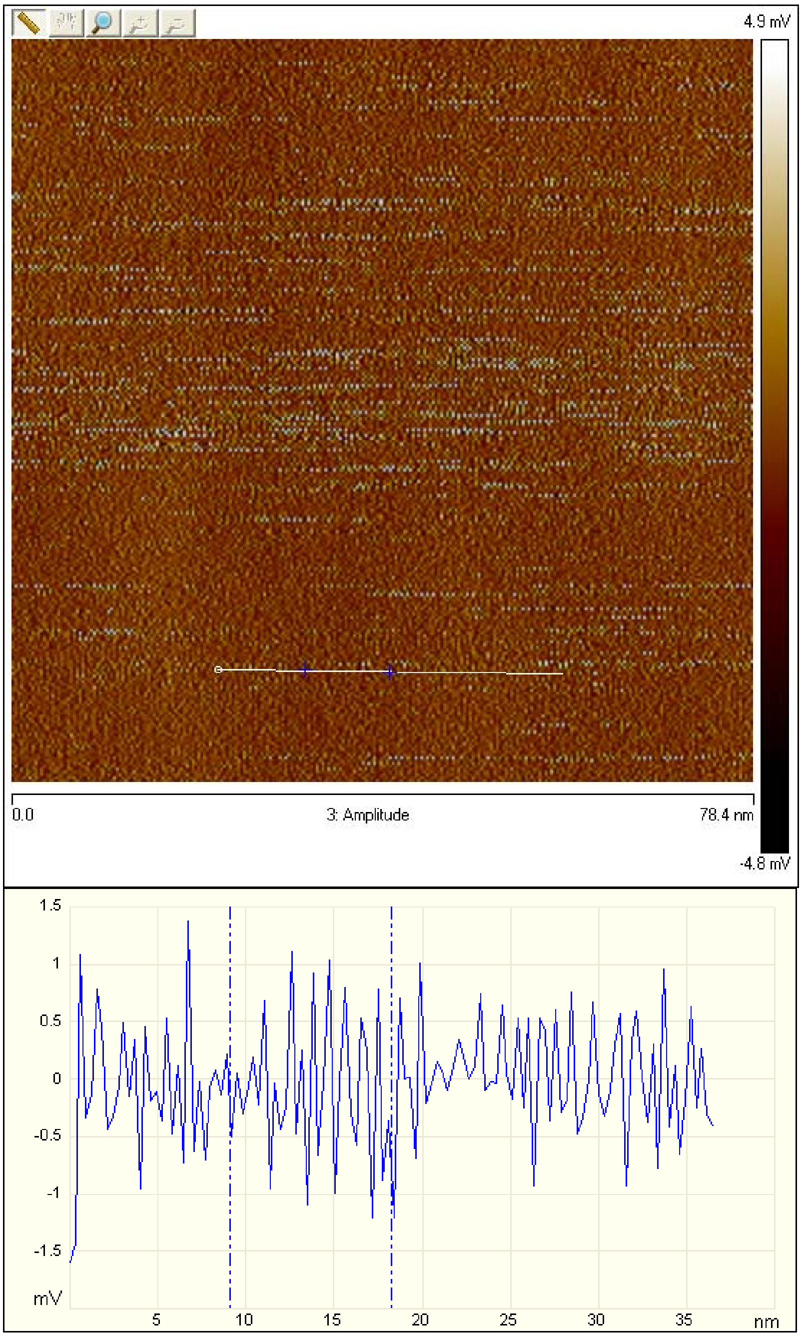

4.9 mV
0.0
3: Amplitude
78.4 nm
-4.8 mV
1.5
1
0.5
0
-0.5
-1
-1.5
mV
5
10
15
20
25
30
35
nm

Fig. S6 Baseline-corrected Raman spectra of the graphene films showing the presence of the 2D band between 2600 and 2900 cm^{-1}. From bottom to top: single-layer, double-layer, four-layer and ten-layer graphene.