Control of size and density of ZnO-nanorods grown onto graphene nanoplatelets in aqueous suspensions

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Keywords: Graphene nanoplateletes, Zinc Oxide nanorods, decorated graphene, aqueous solution growth methods, HR-TEM, XRD, XPS, UPS

Graphene nanoplatelets (GNPs):

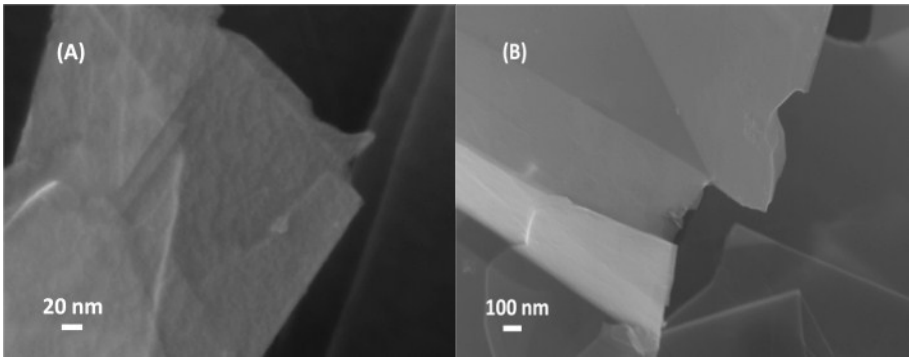

Fig.S1 (A-B) FE-SEM images of GNPs obtained through liquid phase exfoliation in ethanol (sample G).

ZnO-NRs growth onto unseeded GNPs:

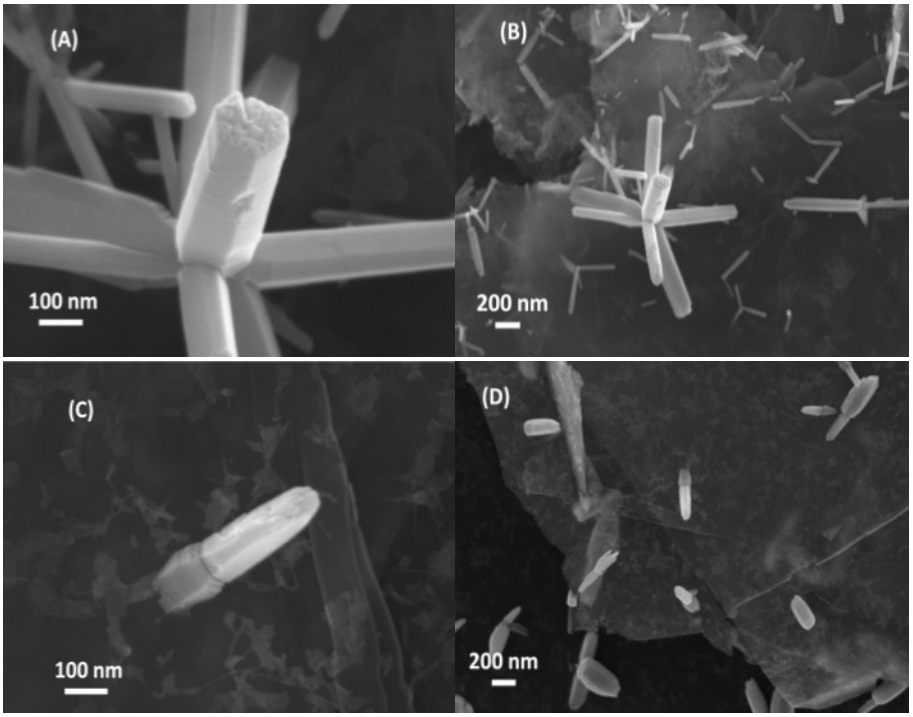

Fig.S2 FE-SEM images of ZNGs obtained by NR growth onto unseeded GNPs by; (A-B) hydrothermal method (sample G-HT1) and (C-D) probe sonication method (sample G-PS).

The seedless growth onto unsupported GNPs dispersed in the growth solution, performed by HT1 and PS methods, has produced the samples G-HT1 and G-PS, respectively. It can be seen from Fig. S2 (A-D), that the growth has taken place in both cases, but it severely suffers from

uniformity and density. Fig. S2 (A-B) indicates that the rods grown by hydrothermal method are characterized by a very low density and wide size distribution. The rods in the sample G-HT1 have the diameter ranging from 32 to 226 nm and lengths ranging from 230 to 747 nm. Fig. S2 (C-D) represents the sample G-PS, in which the rods were grown by probe sonication method. These rods are bulky structures with a very poor coverage having the diameters from 90 to 200 nm (average 145 nm) and lengths ranging from 200 to 409 nm (average 304 nm).

X-ray diffraction (XRD)

Experiment:

(Continuous from Manuscript)… Absorption was modeled according to Sabine et al. 1998.[2] Handling of preferred orientation was performed following the procedure devised by Ballirano (2003).[3] Refinements were performed using the ellipsoid-model of Katerinopoulou et al. (2012),[4] which describe the diffraction-vector dependent broadening of diffraction maxima. In the hexagonal symmetry, the shape ellipsoid parameters b_{ij} are constrained as $b_{11} = b_{22} = 2b_{12}$; $b_{13} = b_{23} = 0$. The ellipsoid is oriented with the principal radii $r_a \perp c$ and $r_c \parallel c$.

Analysis:

Structural information on the analyzed hybrid nanostructures is reported in Table S1. Zincite has the ZnS wurtzite structure, and it is characterized by cell parameters and volume smaller than those of all the nanorods investigated in these studies, in agreement with previous findings on other simple oxides (Di Marco et al., Ballirano et al.)[5-7]. The <Zn-O> bond distance of 1.978 - 1.979 Å obtained for the samples is in perfect agreement with the findings of Sowa and Ahsbahs.[1] Analysis of the micro structural parameters indicates that ε_0 micro-strain (lattice strain), defined as $\beta_i = 4\varepsilon_0 \tan\theta$, β_i being the peak integral breadth (Ballirano and Sadun)[8], takes the larger value of 0.037 - 0.039 in the case of samples G1-HT1 and G1-HT2, whereas it is absent in the case of the sample G2-PS. The latter sample is characterized by a smaller r_c/r_a ratio as compared to those of the HT samples. This observation is in qualitative agreement with the <length>/<diameter> ratios observed from FE-SEM.

Table S1 Cell parameters *a*, *c*, *c*/a, volume, bond distances, and microstructural parameters of the analysed Hybrid ZnO-GNP samples. Reference data SA06[1] from single-crystal analysis are reported for comparison purposes.

	G1-HT1	**G1-HT2**	**G2-PS**	**SA06**
***a* (Å)**	3.25148(3)	3.25093(2)	3.25186(7)	3.2494(2)
***c* (Å)**	5.20681(6)	5.20770(4)	5.20881(17)	5.2054(2)
c/a	1.6014	1.6019	1.6018	1.6020
volume (Å^3)	47.6723(9)	47.6642(6)	47.702(2)	47.598(7)
<Zn-O>	1.978	1.978	1.979	1.978
r_c/r_a	2.58(5)	2.49(5)	2.01(5)	-
ε_0	0.0389(6)	0.0371(4)	0.000(9)	-

Chemical purity analysis by XPS

The chemical composition and chemical states of elements for all the samples are reported in Table S2.

Table S2 XPS quantification and chemical states of all constituent elements.

G1-HT1	**C1s**	**Zn2p$_{3/2}$**	**O1s**		
			A	**B**	**C**
Atomic %.	48.4	23.6	12	11.5	4.4
B.E. (eV)	284.4	1022.3	531.1	532.5	533.8
Bond	graphene	ZnO	oxide	OH groups	adsorbed H_2O
G1-HT2	**C1s**	**Zn2p$_{3/2}$**	**O1s**		
			A	**B**	**C**
Atomic %.	58	20.6	13.3	6.1	2.1
B.E. (eV)	284.4	1022.2	531	532.4	533.6
Bond	graphene	ZnO	oxide	OH groups	adsorbed H_2O
G2-PS	**C1s**	**Zn2p$_{3/2}$**	**O1s**		
			A	**B**	**C**
Atomic %.	67	13.5	8	8.9	2.6
B.E. (eV)	284.4	1022.3	531.1	532.4	533.8
Bond	graphene	ZnO	oxide	OH groups	adsorbed H_2O
Reference (graphite)	**C1s**	**Zn2p$_{3/2}$**	**O1s**		
			A	**B**	**C**
Atomic %.	98.5	---	---	1	0.5
B.E. (eV)	284.4	---	---	532.1	533.7
Bond	graphite	---	---	OH groups	adsorbed H_2O

XPS chemical imaging

Fig. S3 shows the chemical image obtained on sample G1-HT1. It is clearly evident that the Zn 2p signal is homogeneous and densely distributed all over the surface. Similar images were acquired for all other samples.

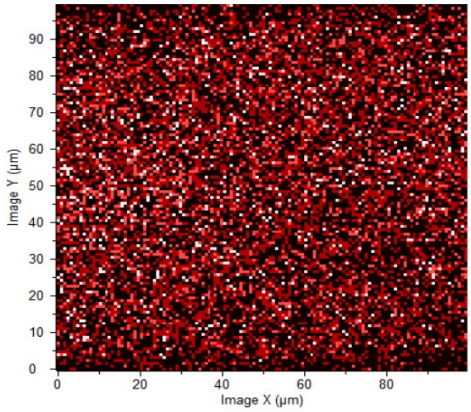

Fig. S3 XPS chemical image of Zn2p acquired for the sample G1-HT1 (dimensions: 100 x 100 μm^2)

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