Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

"Effect of nitriding/nanostructuration of few layer graphene supported iron-based particles; catalyst in graphene etching and carbon nanofilaments growth"

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Morphology of nitrogen containing particles: The statistical TEM analysis depicts the existence of three main types of particles; i.e. core-shell, homogeneous and semi-core-shell particles located at the edges of graphene (Fig.S1).

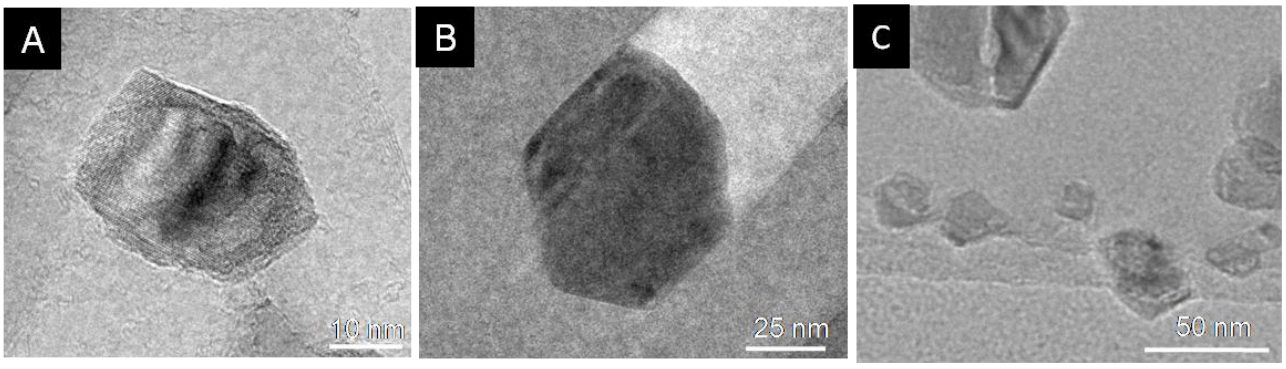

Figure S1. TEM micrographs of faceted nanoparticles obtained after ammonia treatments: A) core-shell, B) homogenous, C) semi-core shell.

Crystallographic investigation:

DRX pattern confirms the formation of iron nitride, although minimum two different FeN_x structures/phases are observed (Fig. S.3):

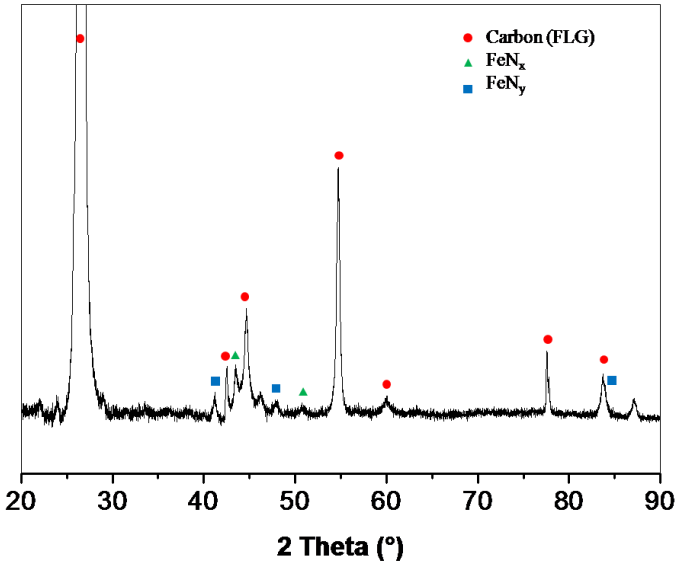

Figure S2. DRX pattern of ammonia treated FLG-supported Fe_3O_4 particles.

The powder X-ray diffraction (XRD) analysis was carried out on a Bruker D-8 Advance diffractometer in the 27-65° (2θ) range with a scan step of 0.03°.

The electron diffraction uncovers a contribution of $Fe_{16}N_2$ to the structure of the particles (Fig. S3).

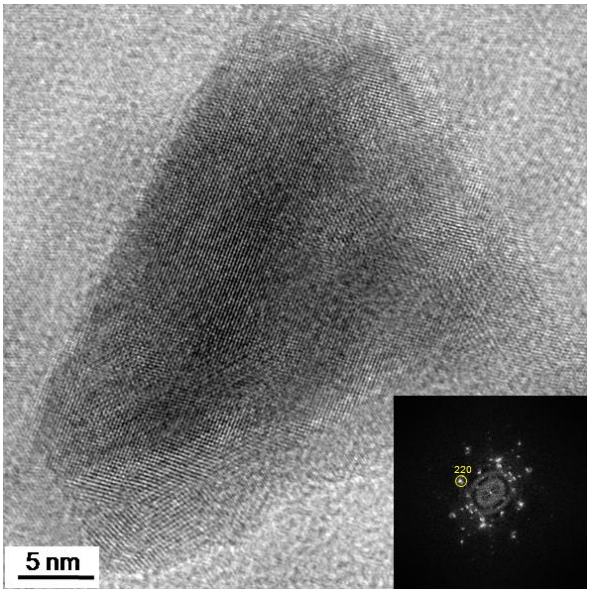

Figure S3. HR-TEM micrograph and electron diffraction of $Fe_{16}N_2$ containing particle (d_{220}=0,214 nm).

Etching of FLG by nitrogen rich particles: The etching of graphene proceeds with reorganization of catalyst and the nitrogen rich core is displaced toward a head of active particles, leaving behind the nitrogen free tail with weakly defined structure for core shell particles. It can be visualized punctually also by standard TEM micrograph (Figure S4):

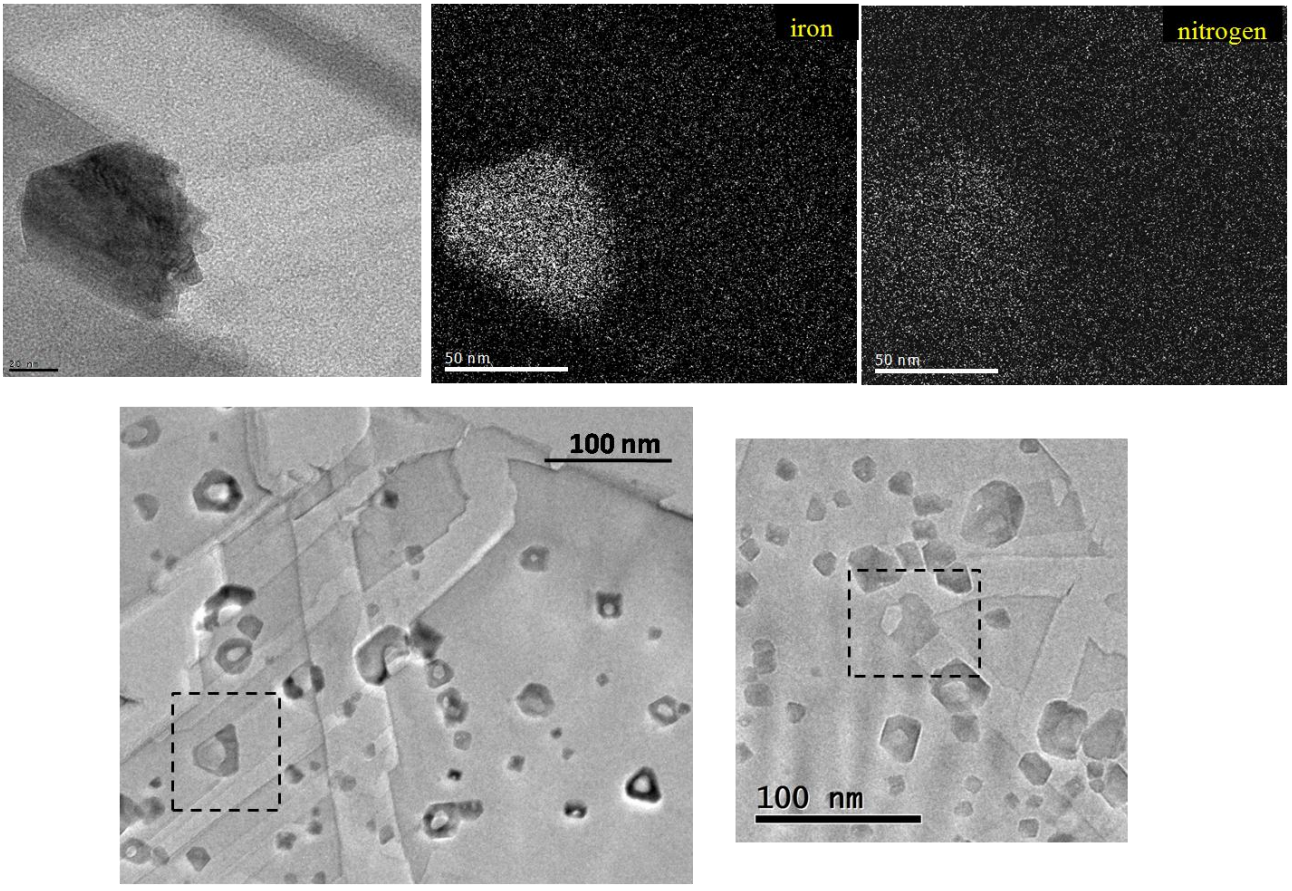

Figure S4. TEM and TEM/EELS analysis micrographs showing a displacement of faceted FeN_x core during etching of graphene.

The figure S5 A and B presents the same image, where two zones of two catalyst-free (acid treatment) FLG assemblies after cutting are distinguished; and the zones are slightly rotated toward each other. The images show that the etching process starts from the edges of FLG sheets and

follows a direction perpendicular to the edges in the first zone (A) and 60° from the edges in the second zone (B), while etched channels are parallel to one another within the zones.

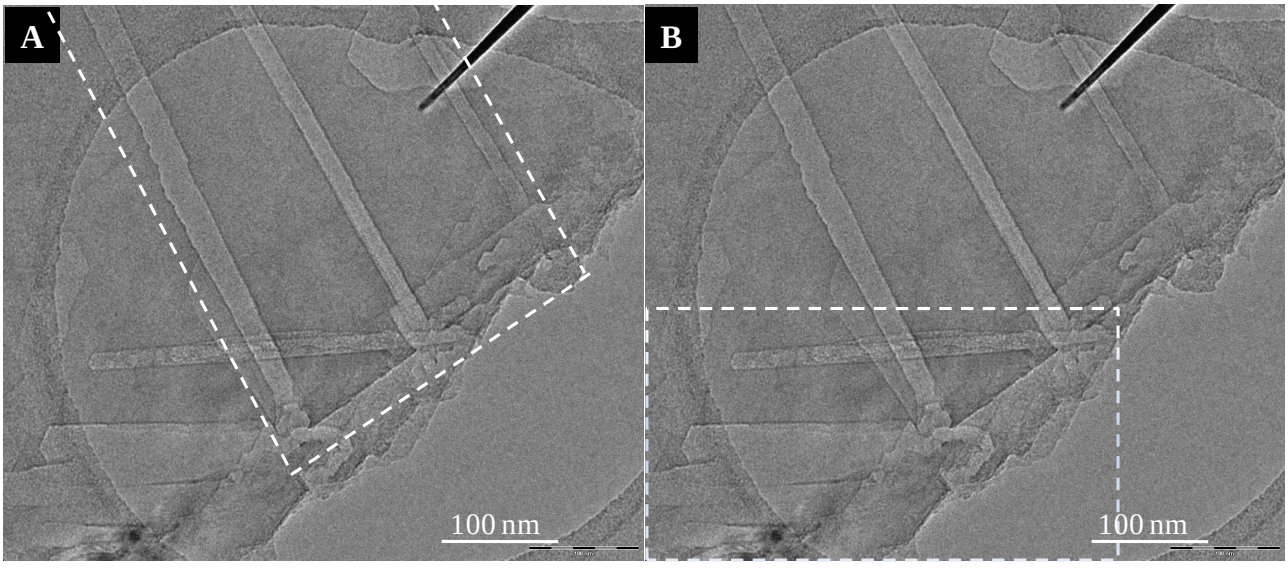

Figure S5. TEM micrograph with two zones (A) and (B) of two catalyst-free FLG assemblies, where graphene etching proceeded with direction perpendicular to the edges in the first zone (A) and at 60° from the edges in the second zone (B).

Formation of CNTs:

Decomposition of ethane performed on reduced at 400°C spherical iron catalyst (Fig. S6A) results in the formation of typical hollow carbon nanotube structures (Fig.S6B).

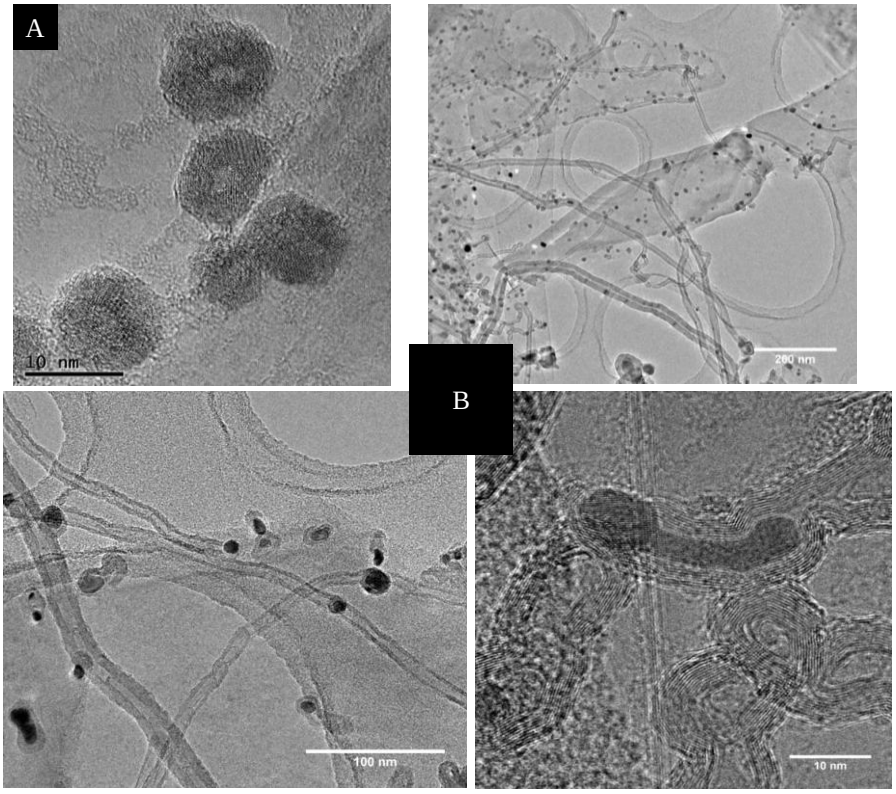

Figure S6. TEM micrographs of Fe_3O_4/FLG catalyst reduced at 400°C with spherical shape of particles (A) and CNTs grown on this catalyst during ethane decomposition at 800°C.