High temperature dynamics of nanocrystalline graphene: a high resolution in situ transmission electron microscopy study

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Graphitization of polymers offers an efficient way to synthesize nanocrystalline graphene on different substrates with tunable shape, thickness and properties[1]. We have extended this approach to study the catalyst free thermal formation of free-standing nanocrystalline graphene films and followed the graphitization using *in situ* TEM techniques, combining atomic and high resolution imaging, diffraction and electron energy loss spectroscopy (figure 1). *In situ* graphitization allowed to understand the chemical and structural evolution of the nanocrystalline graphene during the pyrolysis process. The *in situ* studies showed that the graphitization process is highly dynamic with a number of intermediate reactions leading to the formation of different carbon nanostructures. A two-step growth mechanism was identified in which intermediate temperature (600-1000 C) crystallite growth occurs mostly by consuming amorphous carbon around the crystallites and the high temperatures (1000- 1200 C), the growth proceeds by the merging of crystallites (figure.1). The amorphous carbon transforms in two ways, one by attaching on to the active edges of domains and by the catalyst free transformation on the top of other graphitic layers. This catalyst free transformation forms mobile and stationary (pinned) carbon nanostructures structures with varying size and shape[2].

In situ HRTEM investigations revealed the formation of graphene nano flakes and cage like nano structures during graphitization. The dynamics and interaction of these structures with the graphitic substrate differ a lot and gave insights in to the fundamental processes controlling graphene growth. Small graphitic flake like structures are highly mobile on the graphitic substrate and move/attach to the edges of a graphene flake, extending the flake (figure 2). On the other hand, the cage likes structures, exhibit a stable size but are moving fast owing to the weak interactions with the substrate (figure 2.e-h). The study shows that the growth of the domains is mainly by the migration and merging of the graphitic subunits. In addition to this, strong structural and size fluctuations of individual graphitic subunits at high temperatures are observed. Graphene nano flakes are highly unstable and tend to loose atoms or groups of atoms to adjacent larger domains probably indicating an Ostwald type of ripening in these 2D materials as an additional growth mechanism. Beam off heating experiments were carried out to understand the effect of beam, to separate out the beam induced transformations and the inherent temperature driven mechanisms.

References:

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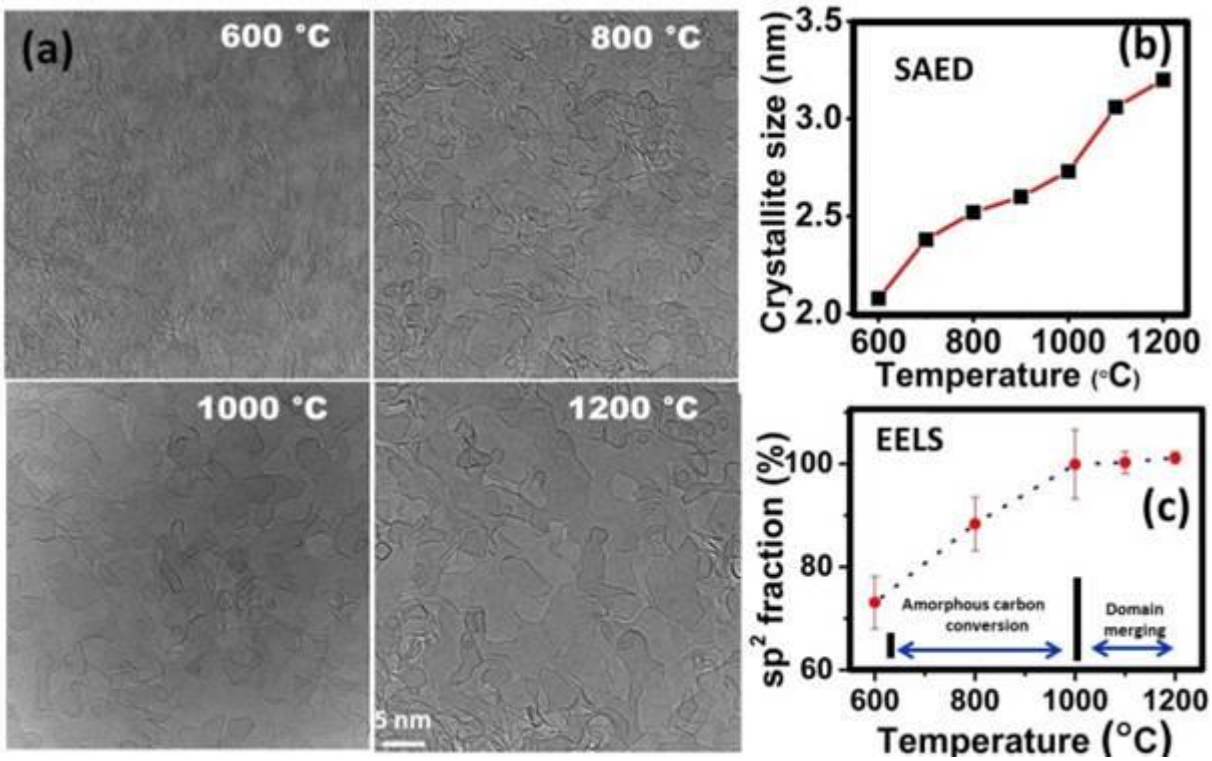

Figure 1: (a) The evolution of domains, (b) crystallite size evolution during hating and (c) the sp^2 carbon content at different temperatures. The sp^2 content increases from 600 C to 1000 C and saturates indicating that the amorphous sp^3 carbon is completely consumed at 1000 C and further domain growth is facilitated by merging of domains.

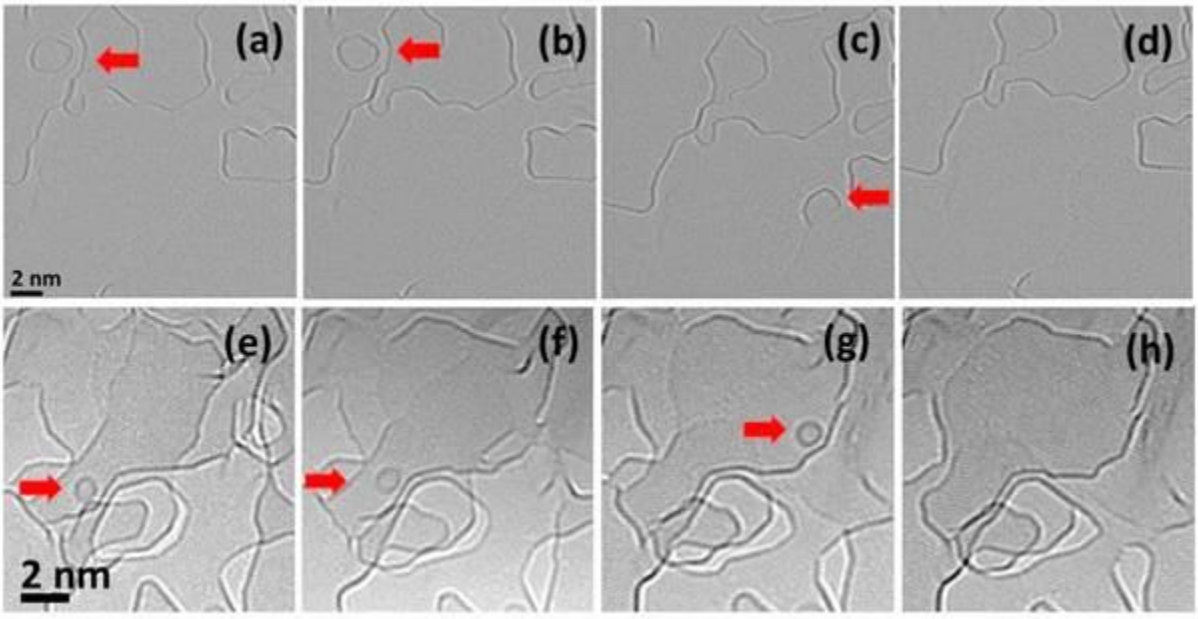

Figure 2: (a-d) Migration and merging of a graphitic flake at 1200 C and (e-h) movement of a cage like structure at 1200 C.