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Structural Stability and Release Behavior of Iron Nanocrystals Encapsulated in Carbon Shells by *in situ* TEM/HRTEM Observation

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Nanocrystals often have novel physical and chemical properties, which differ from those of the corresponding bulk materials. Therefore, metal nanocrystals have wide range of applications such as high-density magnetic data storage, magnetic toners in xerography, magnetic inks and ferrofluids [1-3]. However, the poor oxidation resistance of the bare metal nanocrystals sets a great barricade for further exploring their applications. Carbon-encapsulated metal nanocrystals have aroused great research interests because the protective carbon layers prevent the rapid oxidation of bare metal nanocrystals. In the meantime, graphene-like carbon shell is ideal for surface passivation of the metal nanocrystals, thus this provides structural stability to environment; and it possesses a convenient handle for possible functionalization as well [3].

Graphite-like carbon-encapsulated iron nanocrystals were generated from the catalytic pyrolysis of toluene by ferrocene at 800~1000 ^{o}C. The synthesized graphite-like carbon-encapsulated metal nanocrystals were dispersed on a TEM copper grid for high resolution transmission electron microscopy (HRTEM) (JEOL JEM 2100F) and using Protochip Audra holder to reach 1200^{o}C for *in situ* heating as well as on a silicon nitride membrane window placed into the ultra-high vacuum (UHV) *in situ* TEM (JEM 200 CX) for *real-time* observation from room temperature to the high temperature of 800 ^{o}C. The structural stability of iron nanocrystals encapsulated in carbon shells was investigated by the dynamic observation at high temperature and various electron beam intensity. Structural changes were monitored *in situ* by stream video or slow-scan charge-coupled device (CCD) recording frame by frame.

In situ observation in an electron microscope allows shrinkage of the encapsulated crystals and migration of the atoms through the shells to be monitored [4,5]. Figure 1 shows *in situ* TEM images of iron nanocrystals encapsulated in graphite-like carbon shell at the room temperature, at 600^{o}C and 1200^{o}C. At the room temperature and lower beam current density ~ 50-80 PA/cm^{2}, the nanocrystals are structural stable even with longer irradiation over 1 hour. Nanocrystal iron cores start to migrate out graphite-like carbon shells at the temperature of 400^{o}C and higher temperatures. The iron nanocrystals inside the graphite-like carbon shells shrink continuously until they have completely vanished and pure hollow carbon remain. Larger iron clusters on the surface of the carbon shells can be observed in the temperature range of 600~800^{o}C. At the temperature higher than 800^{o}C and up to 1200^{o}C, the iron clusters on the surface begin to evaporate, and rare iron nanocrystal cores can be observed after heating to 1200^{o}C. At the typical imaging condition with beam current density at ~80 PA/cm^{2}, the surface amorphous carbon layer disappears and the graphite-like carbon shells shrink with graphitic shell number increasing. However, for electron beam current density of 100 PA/cm^{2}, strain of iron nanocrystal cores induced by the contraction of the graphite-like carbon shells and re-crystallization of the iron nanocrystal cores can be observed as shown in Fig. 2. We have shown structural changes/evolution of core iron nanocrystals by electron beam and *in situ* heating. The graphite-like carbon shells provide high-pressure to the inside core metal nanocrystal and *in situ* HRTEM gives unique information of the dynamics of metal nanocrystals.

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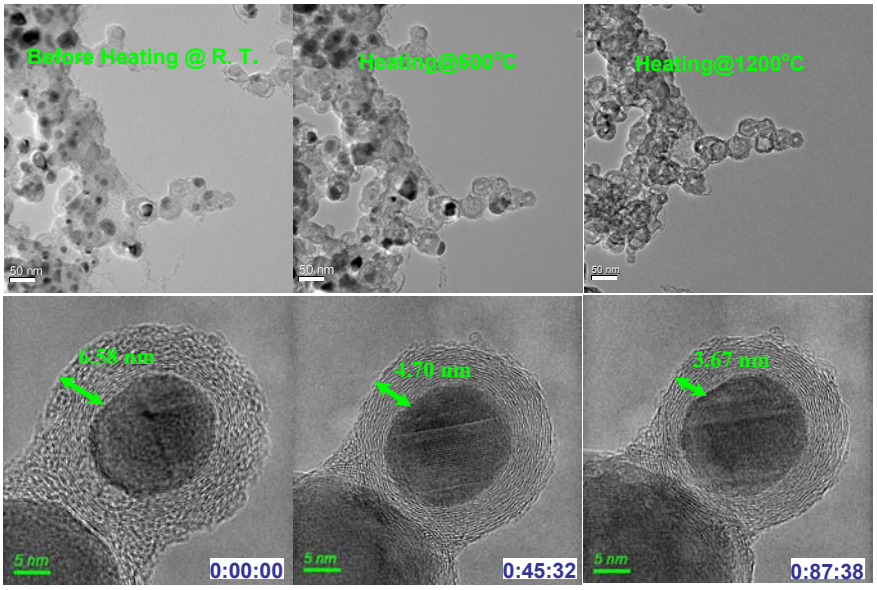

FIG. 1. *In situ* TEM images of carbon encapsulated iron nanocrystals at room temperature, heating at 600°C and further up to 1200°C (upper panel). Sequential HRTEM images of an iron crystals encapsulated in graphite-like carbon shells observed at the typical image beam current density @~80 PA/cm^2 (lower panel).

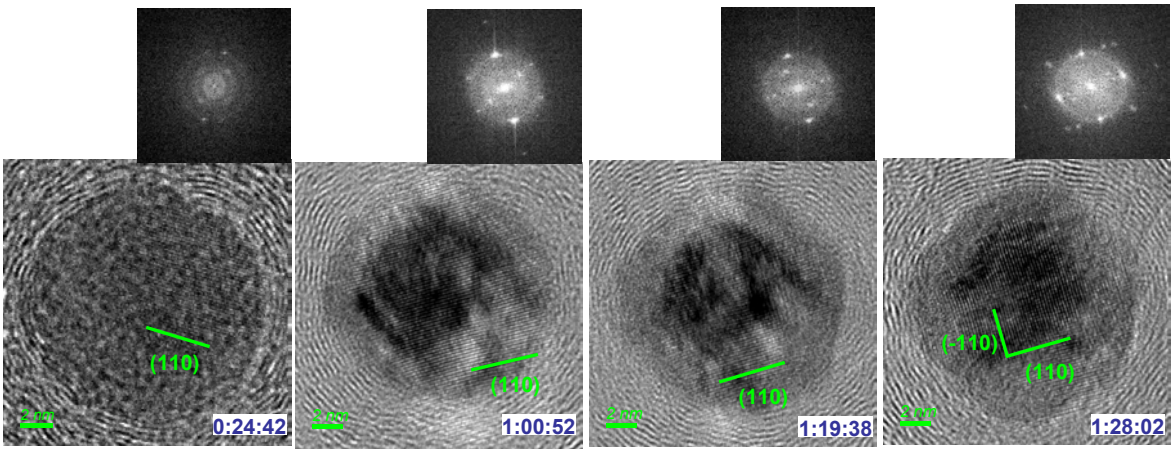

FIG. 2 Sequential HRTEM images showing the evolution of the iron nanocrystal at the increasing beam current density @~100PA/cm^2.

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