Formation mechanism and structural properties of hematite-carbon allotropes nanocomposites: an *in-situ* X-ray diffraction and absorption spectroscopy study

Achievements: The formation mechanism and final structural properties of ultra-small (5 nm) hematite (α-Fe_2O_3) nanoparticles as well as their composites with carbon allotropes such as graphene, graphite and graphene oxide (GO) were assessed by combined XRD and XAS measurements at different temperatures. In particular, the composition of the precursor materials, the transformation temperatures and the temperature stability range of the C-containing compounds were unambiguously determined. In addition, analysis of the Fe K-edge XAS spectra (XANES and pre-peak features) allowed us to investigate the final structural properties of the nano-composites. This information has already been used in order to optimize synthesis procedures of other carbon allotropes-based semiconductor nanocomposites for specific applications in photocatalysis, sensing and energy storage.

Report: XRD measurements of the four precursor samples (iron hydroxide nanoparticles and its composites with graphite, graphene and GO) were carried out at different temperatures in the (25 – 780) K interval, chosen on the basis of previous TGA measurements. Goethite (α-FeOOH) was identified as the only iron hydroxide present in the precursor material giving rise - upon heating - to the above-mentioned composites, with the only exception of the GO-containing sample, where six-lines ferrihydrite was found to be the precursor hydroxide. Combination of XRD and XAS (pre-peak fittings) measurements reveal that these precursors directly transform to hematite. N o intermediate phases or iron oxides different from α-Fe_2O_3 were detected in the investigated temperature range (figures 1 and 2). The transformation of the iron hydroxides into hematite starts at about 475 K, except in the case of the GO composite where it starts near 575 K. In this sample, GO reduction is readily observed and the signal disappears at moderate temperatures. Heating above 600 K increases the nanoparticle size and improves their crystal quality, in agreement with previous Raman spectroscopy measurements.

XAS measurements were performed following the same strategy regarding temperature selection. Deconvolution of the Fe K pre-edge revealed a less centrosymmetric structure in the graphene oxide composite as it has the most intense pre-edge. This is in accordance with previous results, as ferrihydrite is less centrosymmetric than goethite. On the other hand, the centroid position and the pre-edge amplitude reveal that the Fe oxidation state is 3+ in all the samples investigated [1,2]. XANES spectra reveal that in all the cases the atomic distance between Fe-O is in good accordance with that reported in the literature for iron oxides (~1.9Å) [2,3] (phase correction has been taken into account). We were also able to study the evolution of the structural disorder monitoring the relative intensity of the second EXAFS peak (second shell contribution). The obtained results are in good agreement with those obtained by XRD. When the well-crystallized precursor hydroxides are heated, the composite progressively loses its structural order until reaching the temperature where the phase transformation

(to hematite) gets started, i.e., 475 – 575 K depending on the sample considered. From such temperature to 780 K, the structural order is gradually recovered as the hematite phase is formed (figures 1b and 2b).

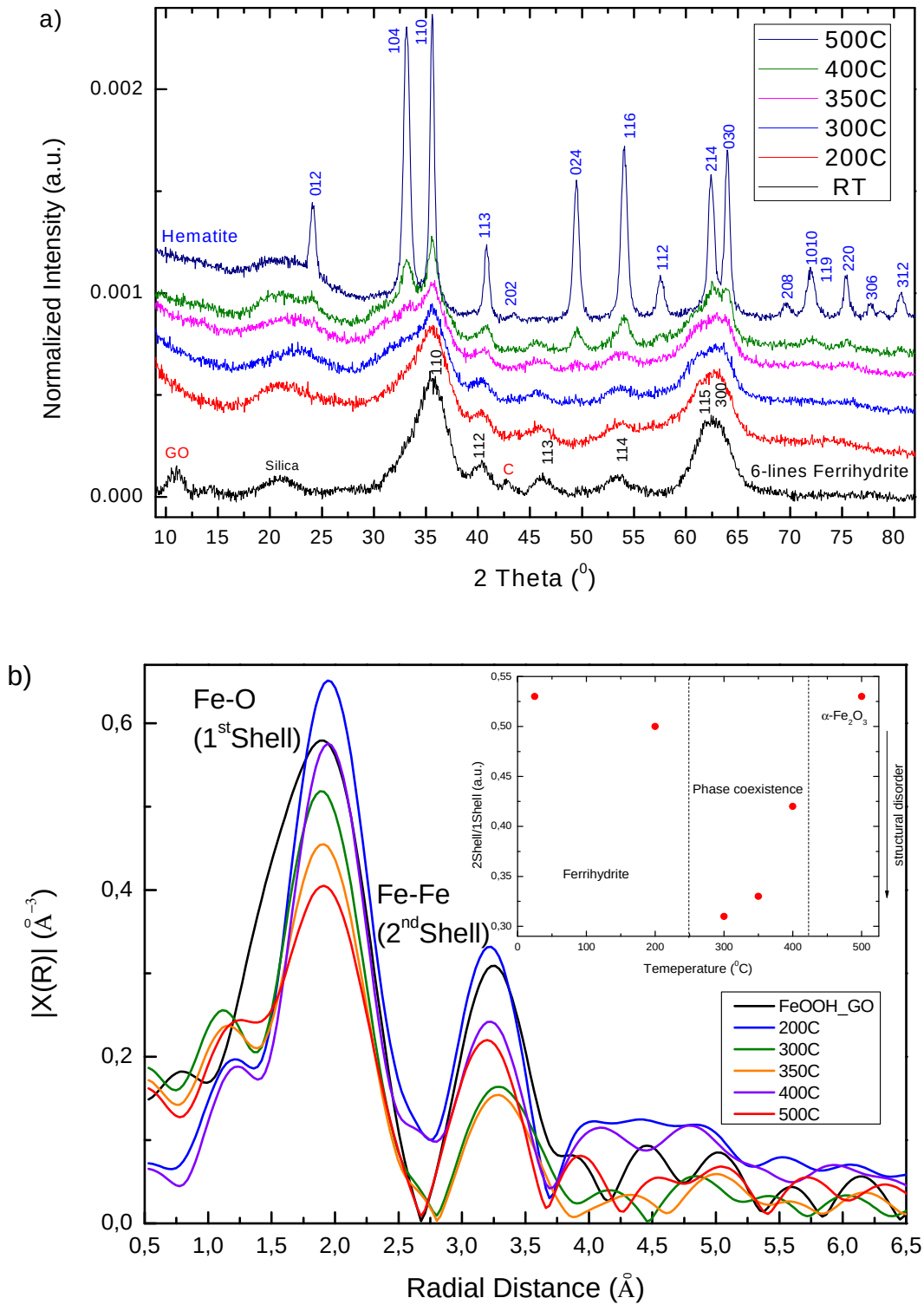

Figure 1. Temperature evolution of the GO - iron hydroxide composite: a) XRD, b) EXAFS (Radial Function Distribution). The inset shows the variation of the relative intensity of the second peak contribution with temperature.

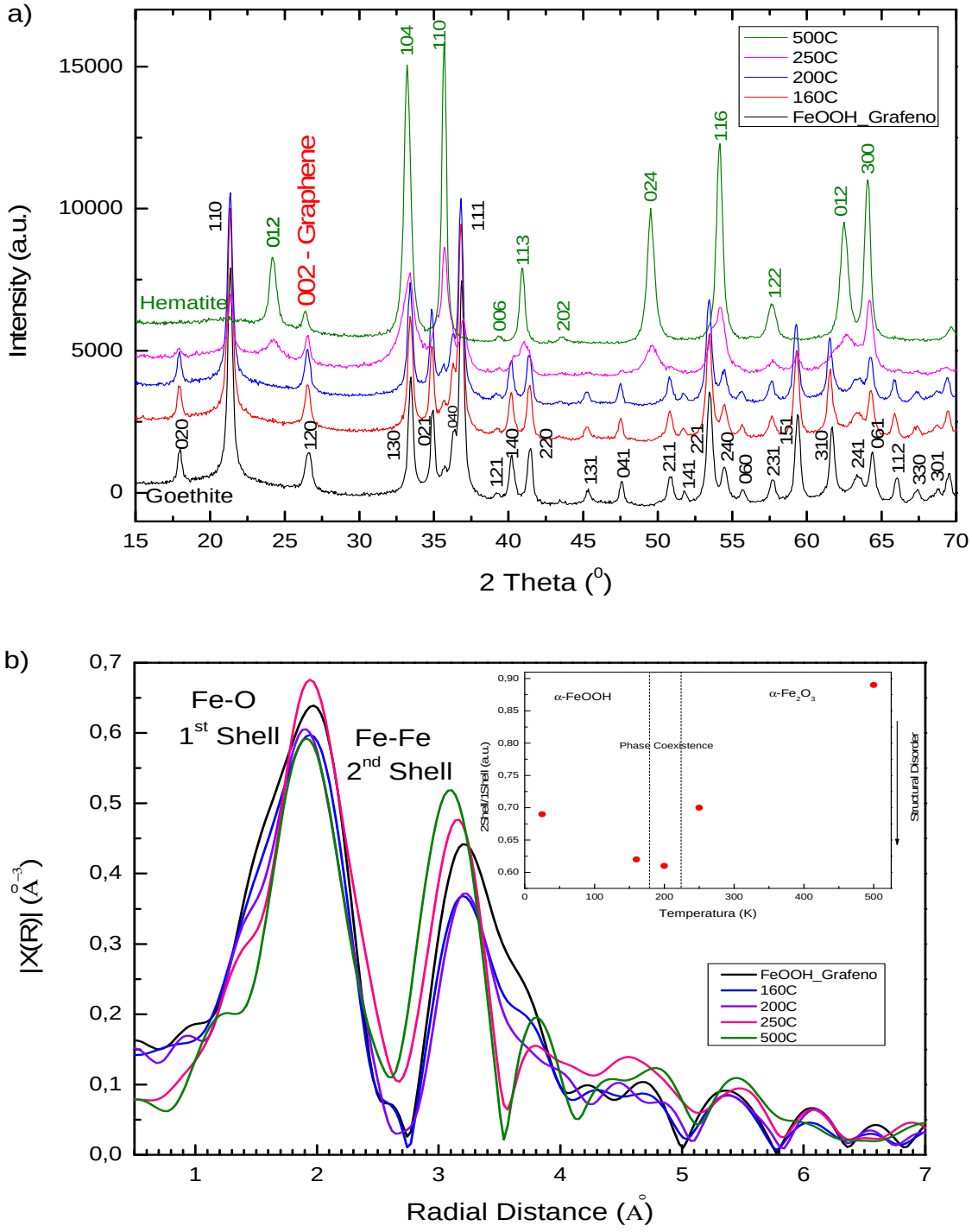

Figure 2. Temperature evolution of the graphene - iron hydroxide composite: a) XRD b) EXAFS (Radial Function Distribution). The inset shows the variation of the relative intensity of the second peak contribution with temperature.

References:

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