

Supplementary Information for

Direct Growth of the Oriented Nanocrystals of Gamma-Iron on Graphene Oxide Substrate. The Detailed Analysis of the Factors Affecting Unexpected Formation of the Gamma-Iron Phase.

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1. The temperature program

The temperature program for the thermal reduction of the carbon-iron composite is direct heating under a nitrogen atmosphere to a temperature of 800 ° C, followed by a 2-hour isotherm and forced cooling to room temperature (RT- (60min) -800 ° C - isotherm (2 hour) - (60min) -RT.

2. Characterization of the samples prepared with alternative carbon sources

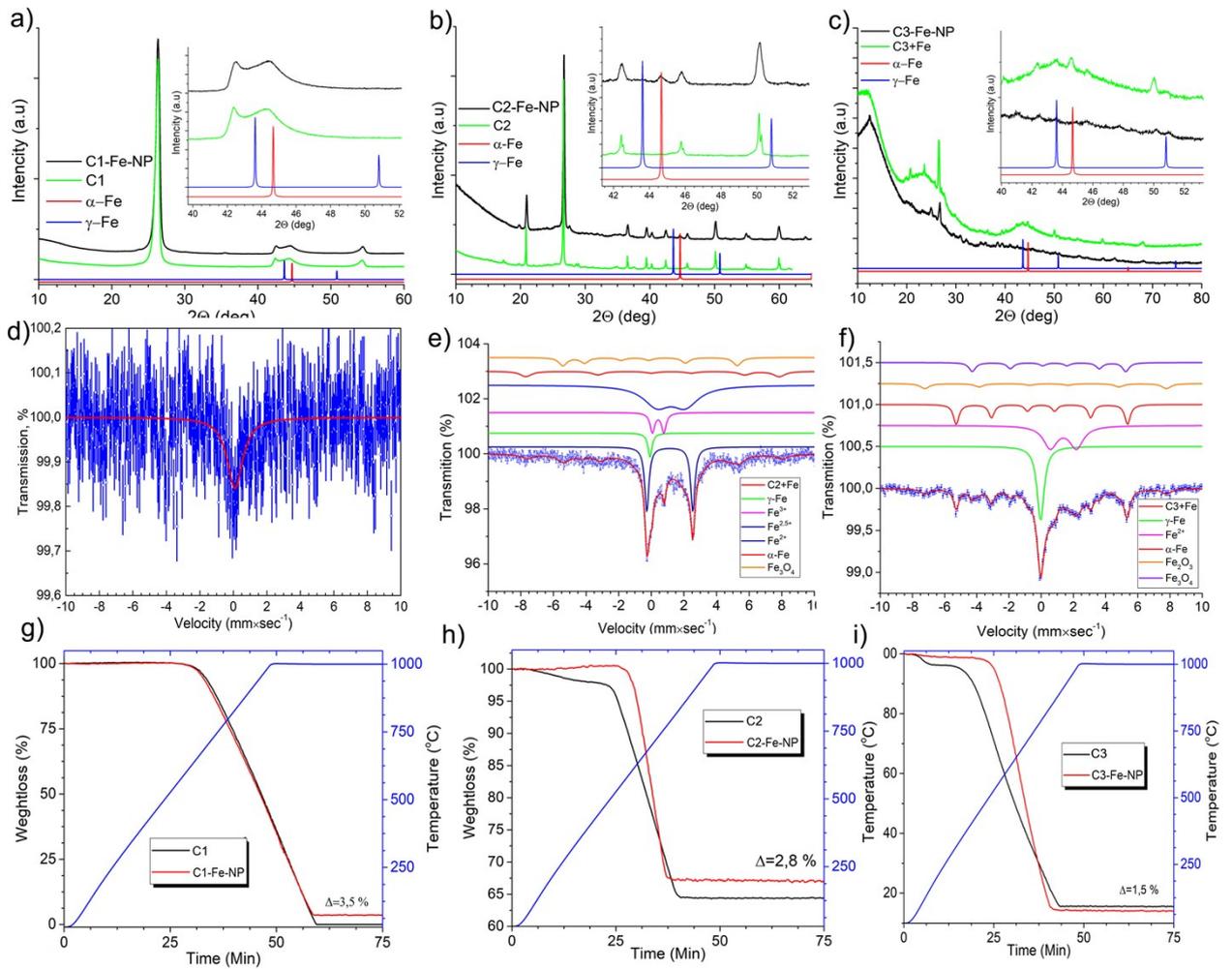


Fig. S1: a) XRD spectra of C1 and C1-Fe-NP ; b) XRD spectra of C2 and C2-Fe-NP ; c) XRD spectra of C3 and C3-Fe-NP ; d) Mössbauer spectra of C1 and C1-Fe-NP ; e) Mössbauer spectra of C2 and C2-Fe-NP ; f) Mössbauer spectra of C3 and C3-Fe-NP ; g) TGA curves for C1 and C1-Fe-NP ; h) TGA curves of C2 and C2-Fe-NP after temperature reduce; i) TGA curves of C3 and C3-Fe-NP ;

The Mössbauer spectroscopy confirms presence of alpha iron in samples, formed from C2 and C3 (Fig. S1 e-f). In addition, an oxide phase is present in them, which corresponds to Fe₂O₃. Another signal can be attributed to complex oxides of the inorganic phase in the mineral shungit (C2), which include alkali and alkaline earth metal ions in the crystal lattice. The remaining signals (Fig. S1 e,f) refer to Fe²⁺, Fe^{2.5+} and Fe³⁺. All these ions constitute the crystal structure of the inorganic phase present in the original carbon source(s). The broad doublet in both spectra can be attributed to mixed iron carbides, which we observed earlier.

For OMC-1, a fully preserved structure of the carbon lattice (Fig. S2a) and weak reflections of two different iron oxides are observed: Fe_2O_3 (110) at $36^\circ 2\theta$ and Fe_3O_4 (220) at $32^\circ 2\theta$ angles. More pronounced differences are observed between the samples with respect to their Mössbauer spectra. In OMC1-Fe-NP, there is a singlet with $\text{IS} = 0.44$ (Fig. S2d), which cannot be attributed to the gamma phase, and most likely belongs to complex iron carbides. Also, in the spectrum there is a strong signal corresponding to the octahedral Fe_3O_4 . In OMC2-Fe-NP, the α -Fe signals are not observed (Fig. S2b). Weak signals of the iron oxide forms are observed in the range from 27 to $40^\circ 2\theta$ angles, and they are originated by the crystal structures of the inorganic phase of the mineral shungit (C2).

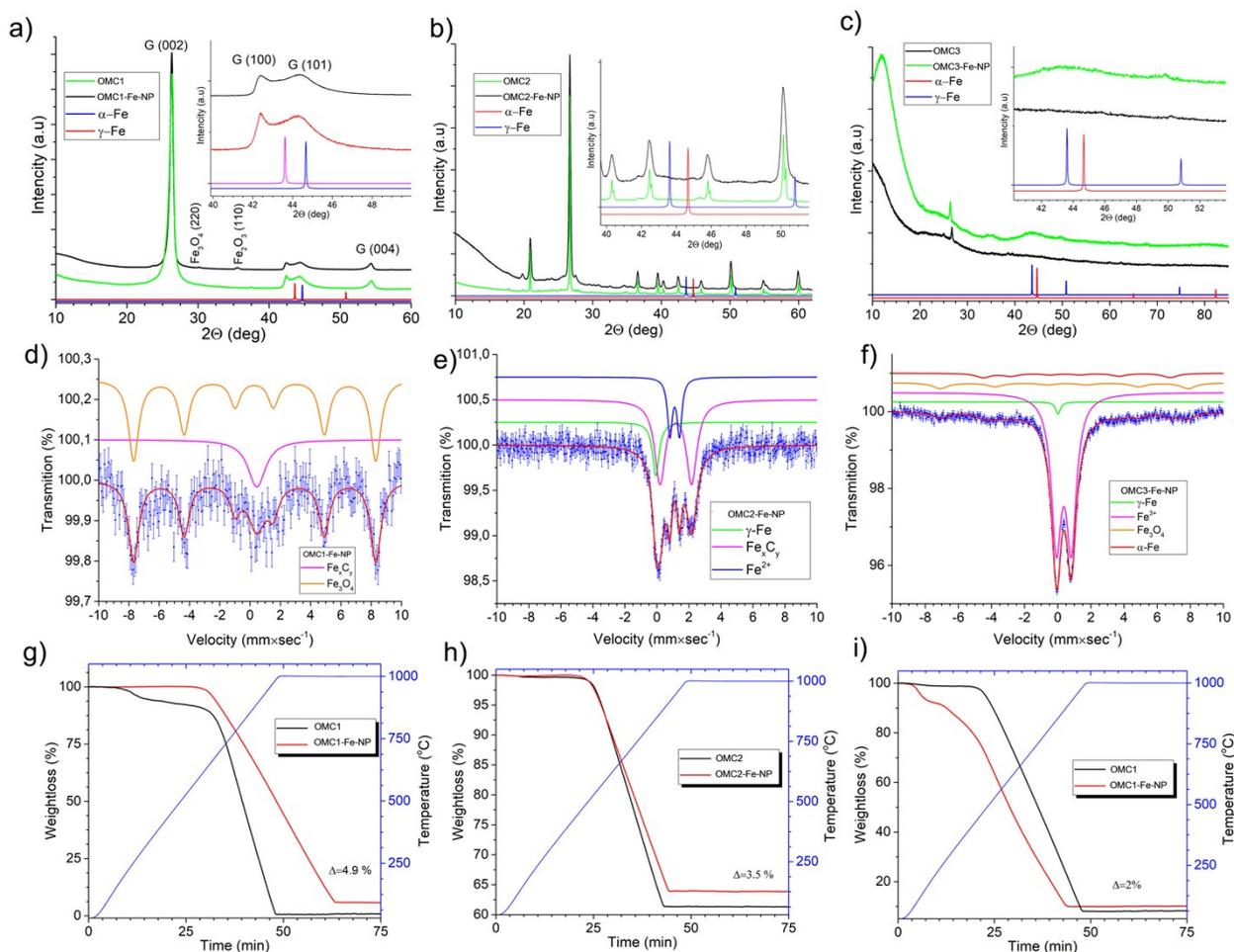


Fig. S2 a) XRD spectra of OMC1 and OMC1-Fe-NP; b) XRD spectra of OMC2 and OMC2-Fe-NP; c) XRD spectra of OMC3 and OMC3-Fe-NP; d) Mössbauer spectra of OMC1 and OMC1-Fe-NP; e) Mössbauer spectra of OMC2 and OMC2-Fe-NP; f) Mössbauer spectra of OMC3 and OMC3-Fe-NP; g) TG curves of OMC1 and OMC1-Fe-NP after temperature reduce; h) TG curves of OMC2 and OMC2-Fe-NP after temperature reduce; i) TG curves of OMC3 and OMC3-Fe-NP after temperature reduce;

In the OMC2-Fe-NP Mössbauer spectra, 3 main signals are observed in the spectra (Fig. S2e): the γ -Fe singlet (10%), and 2 doublets. The first corresponds to the bivalent iron, which probably forms part of the inorganic phase of shungite. The second can be attributed to iron carbides. In the XRD spectra of OMC3 (Fig. S2c), the signals of metal phases of iron are not observed. Almost complete preservation of the structure of the initial carbon are observed.

In OMC3-Fe-NP, the four signals are observed in the Mössbauer spectra (Fig. S2f): a very weak singlet ($\sim 2\%$ of total iron content), which can be attributed to austenite, a strong singlet that can be attributed to Fe^{3+} , and the two sextets, attributable to α -Fe and octahedral Fe_3O_4 . It is also worth noting that, despite the functionalization of the surface, the amount of iron absorbed is not large, varying from 2 to 5% (Fig. S2g-i).