The Role of Graphene-Oxide in Stabilizing the Structure of the High-Temperature γ-Fe Phase

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ABSTRACT

We describe formation of γ-iron nanoparticles with the face-centered cubic structure. In bulk the γ-iron phase is formed above 917°C and transforms into the thermodynamically favored α-phase upon cooling. In present work we demonstrate the unexpected room-temperature stability of the γ-phase of iron in the form of nanoparticles on graphene oxide support with diameters of up to 200 nm. X-Ray diffraction and Mössbauer spectroscopy undoubtedly confirm the stability of the γ-phase at room temperature.

INTRODUCTION

Metal nanoparticles (NPs) on a structural support have gained significant attention in recent years as novel systems for new generations of catalysts, electrode materials in the energy conversion/storage devices. [1-2]

Graphene oxide (GO) is most suitable for the growth of metal nanoparticles because it serves as a

- **Template**
- **Stabilizer**
- **Reducing agent [1-3]**

Among other metals, iron attracts constant attention due to its low cost and peculiar electro-magnetic and catalytic properties. Iron allotropes possess either the body-centered cubic (bcc) or the face-centered cubic (fcc) structure (Fig. 1). Up to 917 °C, iron exists in its α-form (α-Fe). At 917°C, bcc transforms into the fcc lattice, and this allotrope is termed as γ-iron (γ-Fe) (austenite).

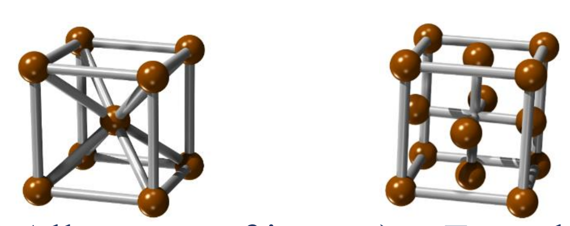


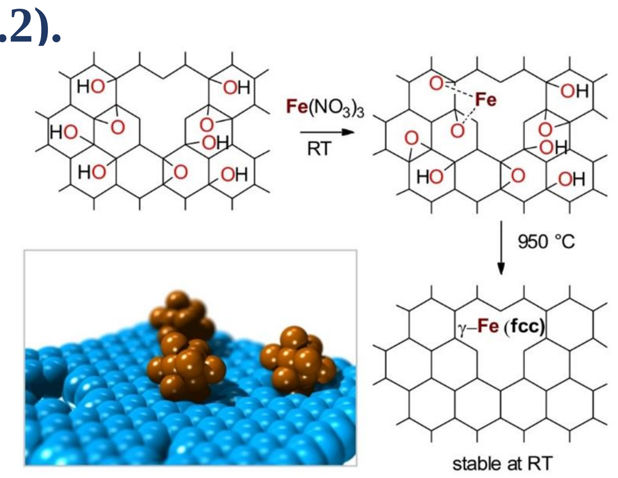
Fig. 1 Allotropes of iron: a) α-Fe and b) γ-Fe

Here, we show the stabilization of the γ-Fe allotrope NPs at room temperature on thermally processed GO. In previous works [4-6] thermal annealing of the variety of iron containing compounds in presence of GO yields mostly iron oxides and iron carbide. Only few studies report on the formation of α-Fe along with iron oxides. [7-8].

MATERIALS

γ-Fe NPs were synthesized in a two-step procedure: first, Fe^{3+} is complexed with oxo-functional groups present on the surface of GO, and second, γ-Fe NPs are formed upon thermal annealing. Metal reduction was carried out by thermal annealing **(Fig.2).**

Fig. 2 Formation mechanism of iron nanoparticles stabilized on thermallyprocessed graphene oxide [9]



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RESULTS

First step: liquid phase reaction to produce Fe^{3+}/GO nanocomposite: Fe^{3+} reacts with oxo-functional groups present on the surface of GO. Mössbauer spectrum of this sample (Fig. 3).

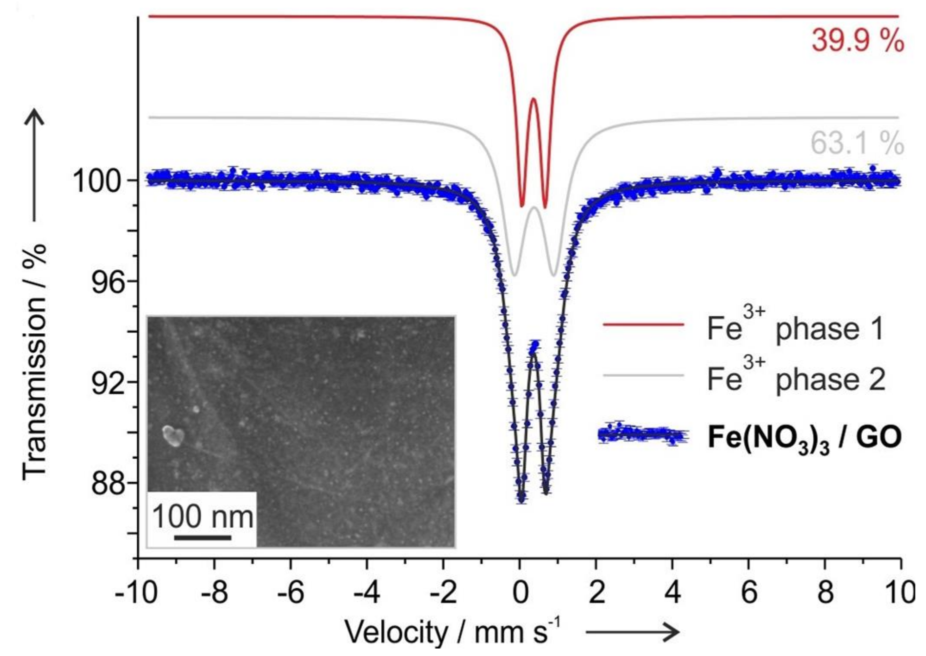

Fig. 3 Mössbauer spectrum (dotted blue line) and deconvolution into two components (red and light-gray lines) before anneling. The inset is the SEM image of the sample.

Table 1. The content of different types of iron in the samples annealed at different temperatures; based on the Mössbauer spectroscopy data.[a]

T / °C	paramagnetic Fe^{3+}	Fe^{2+}	$Fe^{2.5+}$	Magneti-cally ordered Fe-oxides	α-Fe	Fe_xC_y	γ-Fe
RT	100						
300	44.5	40.0		15.5			
600	34.7	1.9		63.4			
700	31.2		30.1	4.7	25.3		8.7
800				4.4	52.1	22.5	19.5
900					35.0	15.6	49.4
950					11.8	22.1	66.1

[a] Iron phases (content in %)

Second step: formation of γ-Fe nanoparticles upon thermal annealing.

- **The γ-Fe nanoparticles begin to form already at a temperature of 700°C. (Fig. 4 - 5)**

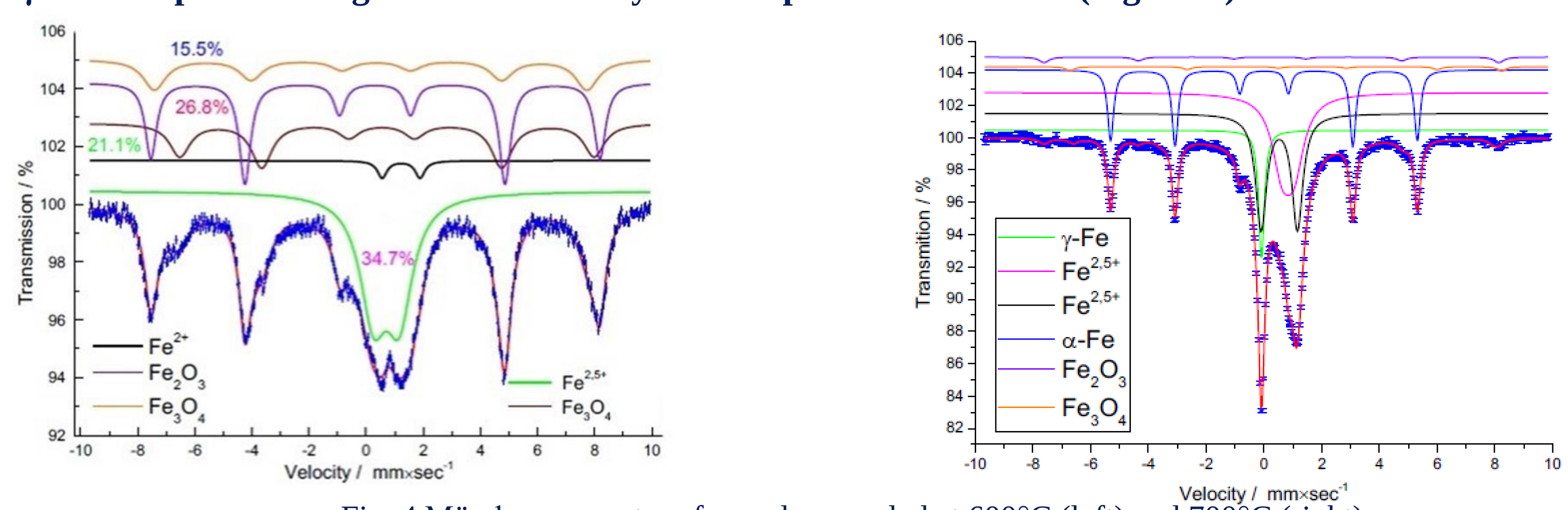

Fig. 4 Mössbauer spectra of sample annealed at 600°C (left) and 700°C (right).

- **Iron oxides are reduced to metallic iron by annealing at temperatures above 800°C. (Fig. 5 -6)**

Fig. 5 XRD patterns for samples annealed at 700°C (left) and 800°C (right).

- **The maximum amount of γ-Fe nanoparticles is obtained by annealing at a temperature of 950°C. (Fig. 6 and Table 1)**

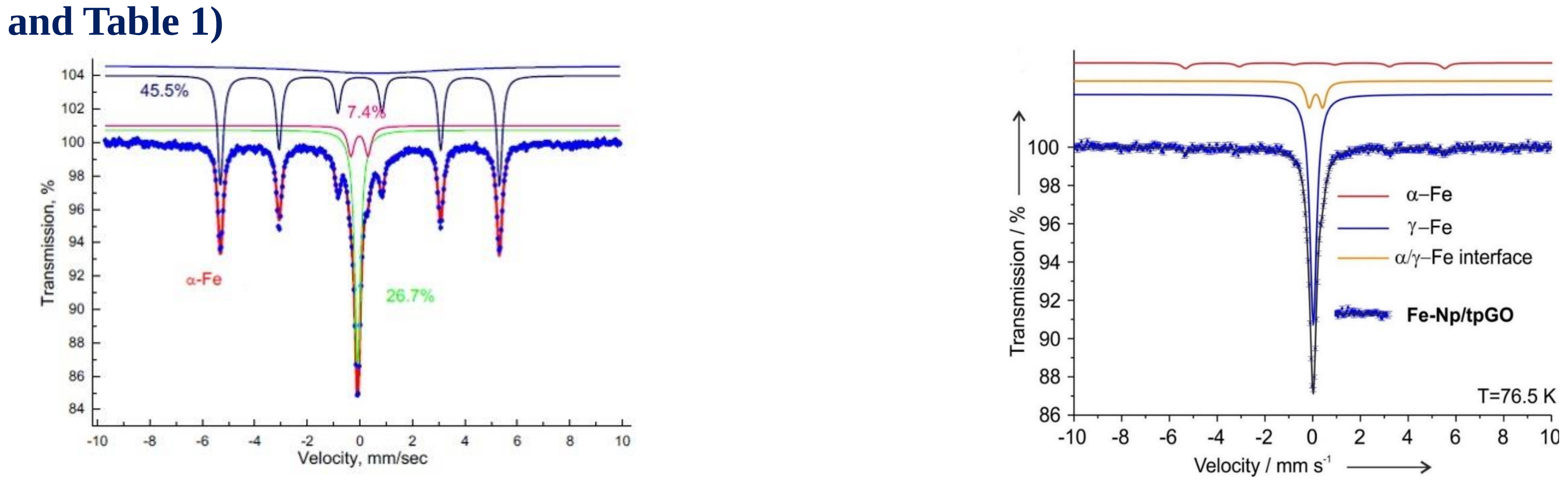

Fig. 6 Mössbauer spectrum (left) of sample annealed at 800°C and acquired at 76.5 K (right) of sample annealed at 950°C.

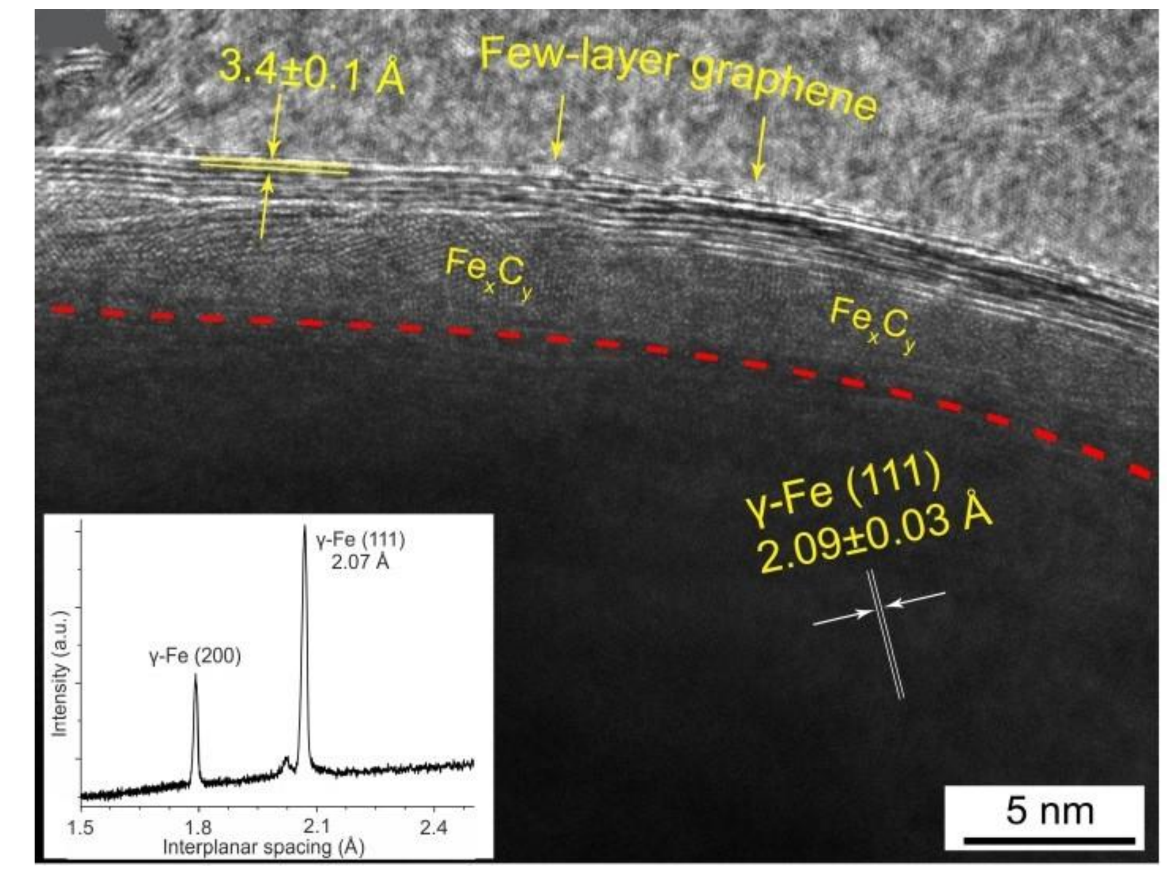

Fig. 7 TEM image of sample annealing at 950°C

CONCLUSIONS

- **The using of graphene oxide (GO) allows the synthesis of γ-Fe nanoparticles, which are stable at room temperature.**
- **GO plays the role of the nucleating site, the reducing agent, the carbon source, and the stabilizer for the formed γ-Fe nanoparticles.**
- **X-ray and Mossbauer measurements have established that the γ-Fe nanoparticles begin to form already at 700°C temperature.**
- **The iron oxides formed during the synthesis can be reduced to metallic iron by annealing at temperatures above 800°C.**
- **The maximum amount of γ-Fe nanoparticles is obtained by annealing at 950°C temperature.**

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