Supporting Information

Expansion of Metal Redox Methodology: The Case of Iron Gallium

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Materials and Methods:

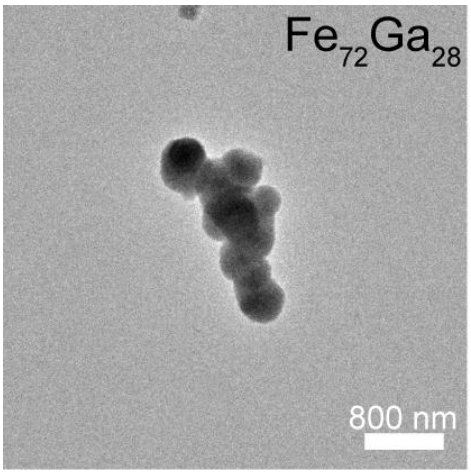
1-Octadecene (ODE, 90%), Toluene (ACS Grade), Acetone (ACS Grade), Fe(CO)5 (99.99%), $Ga(acac)_3$ (99.99%), Trioctylphosphine oxide (90% technical grade), Oleylamine (70% technical grade) were obtained from Sigma-Aldrich and used as received. For a standard Schlenk-line synthesis, 8 mL of ODE (degassed with argon) and desired ligand was loaded into a 3-neck round bottom flask vacuum/purge with argon and was heated up to desired reaction temperature. Airtight vials were loaded with 0.25 mmol $Ga(acac)_3$ and then 2 mL of ODE was added. This solution was bubbled with argon for 10 min and then heated on a stir plate at 85 °C. Once temperature was reached in 3-neck flask, the $Ga(acac)_3$ solution and 0.5 mmol of $Fe(CO)_5$ were rapidly injected simultaneously and allowed to react for 1 hour. After reaction particles are washed with Toulene/acetone mixture and centrifuged at 4000 RPM for 10 min. This wash is completed 2 more times to remove any excess ODE and ligand and remaining metal salts. Sample is then moved to a nitrogen drybox where it is kept for further characterization. Samples were annealed at 550 °C for 12 hours in a 10/90 mixture of H2/N2 atmosphere

prior to magnetization and XRD measurements to increase crystallinity and remove any oxidation that occurred during cleanup.

Room temperature X-ray powder patterns were obtained on a Bruker proteum diffraction system equipped with Helios multilayer optics, an APEX II CCD detector and a Bruker MicroStar microfocus rotating anode X-ray source operating at 45 kV and 60 mA. Transmission electron microscope (TEM) images were obtained using a Field emission FEI Tecnai F20 XT. Size distributions of particles were done by measuring an average of 60 particles over different micrographs to calculate distribution. The magnetic hysteresis (M-H) loops were taken on a Microsense EZ7 vibrating sample magnetometer. A MTI GSL-1100X tube furnace was used for reductive sintering.

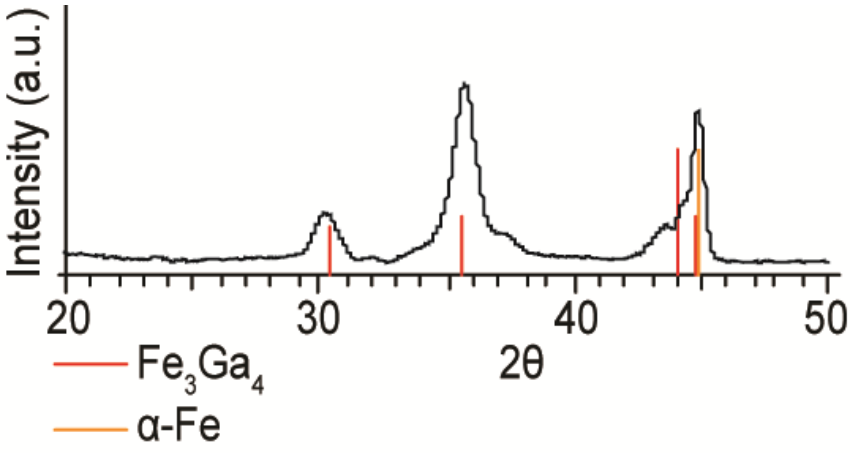
Van't Hoff Plot and Equilibrium Constant

A simplified reaction equation can be thought of $Fe^0 + Ga(acac)_3 \rightleftharpoons Ga^0 + Fe(acac)_3$. With this a equilibrium constant (K) can be determined by $[Ga^0]/[Fe^0]$ which can easily determined by EDS of the final nanocomposite. Finding K for each different temperature, then the Van't Hoff equation can be constructed by using $Ln(K) = -(\Delta H/R)(1/T) + \Delta S/R$, where the ΔH and ΔS are the enthalpy and entropy change, R is the gas constant and T is the reaction temperature. The linear line fitted can then be used to solve for any equilibrium constant within the temperature window, which is directly related back to the stoichiometry in the final particles.

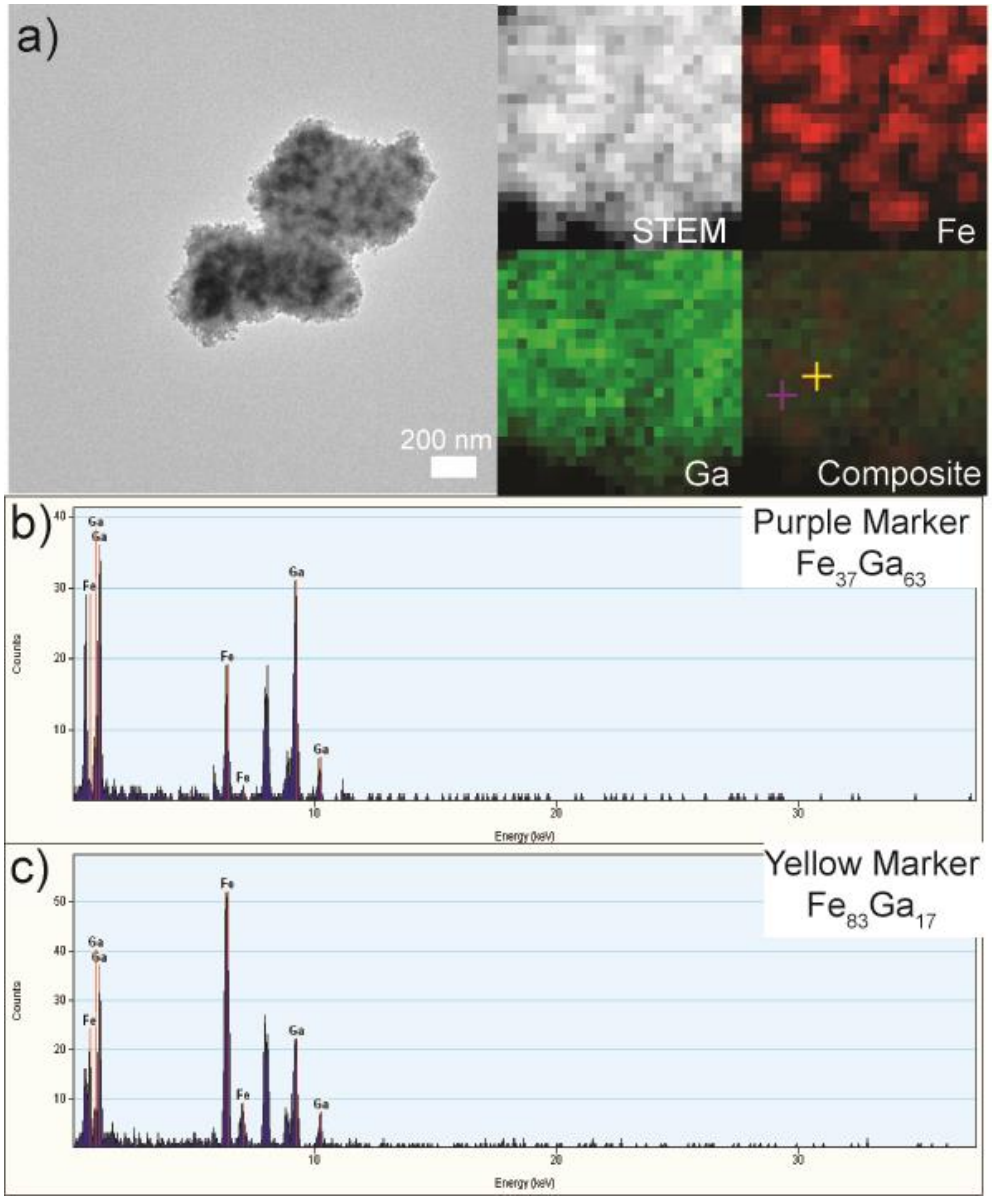


S.I. Figure 1. TEM image of FeGa nanoalloy produced at 300 °C and 4 hour reaction time.

To study if the reaction reached equilibrium within the 1 hour reaction time, a standard reaction of 300 °C was ran for 4 hours. Particles produced from this reaction are displayed in S.I. Figure 1 showing similar size and composition to the nanoalloys produced in the main text. It is believed that 1 hour is enough time to reach equilibrium and that the reaction is not kinetically limited.



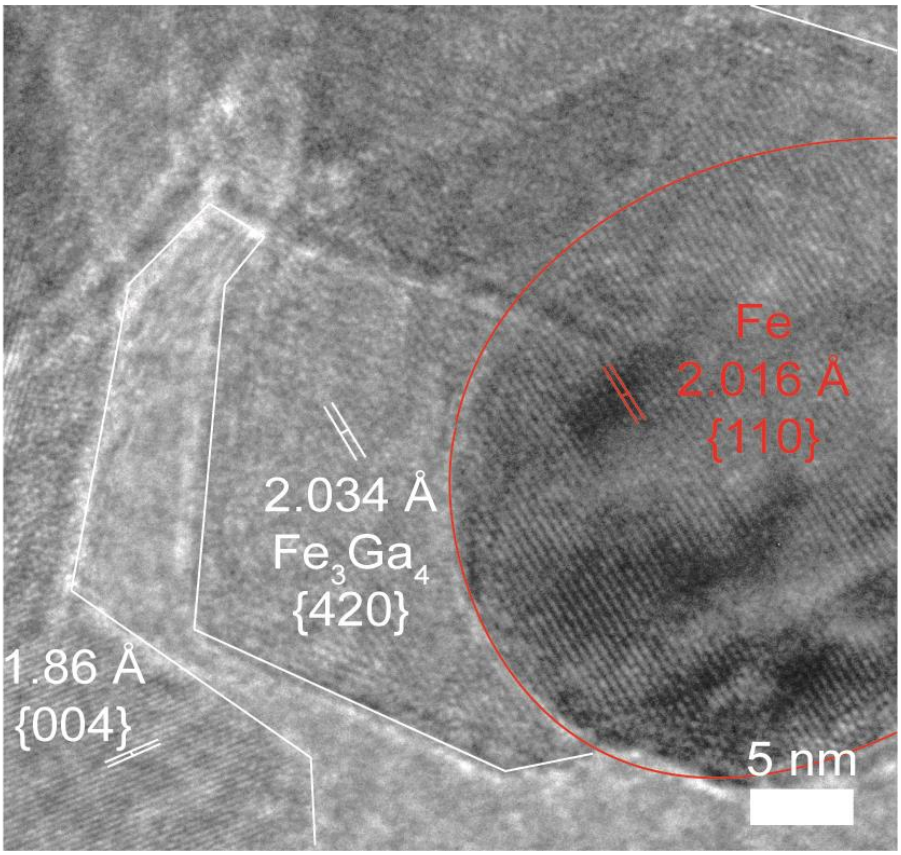
S.I Figure 2. XRD spectra of FeGa nanoalloy annealed at 800 °C for 1 hour displaying two-phase formation.



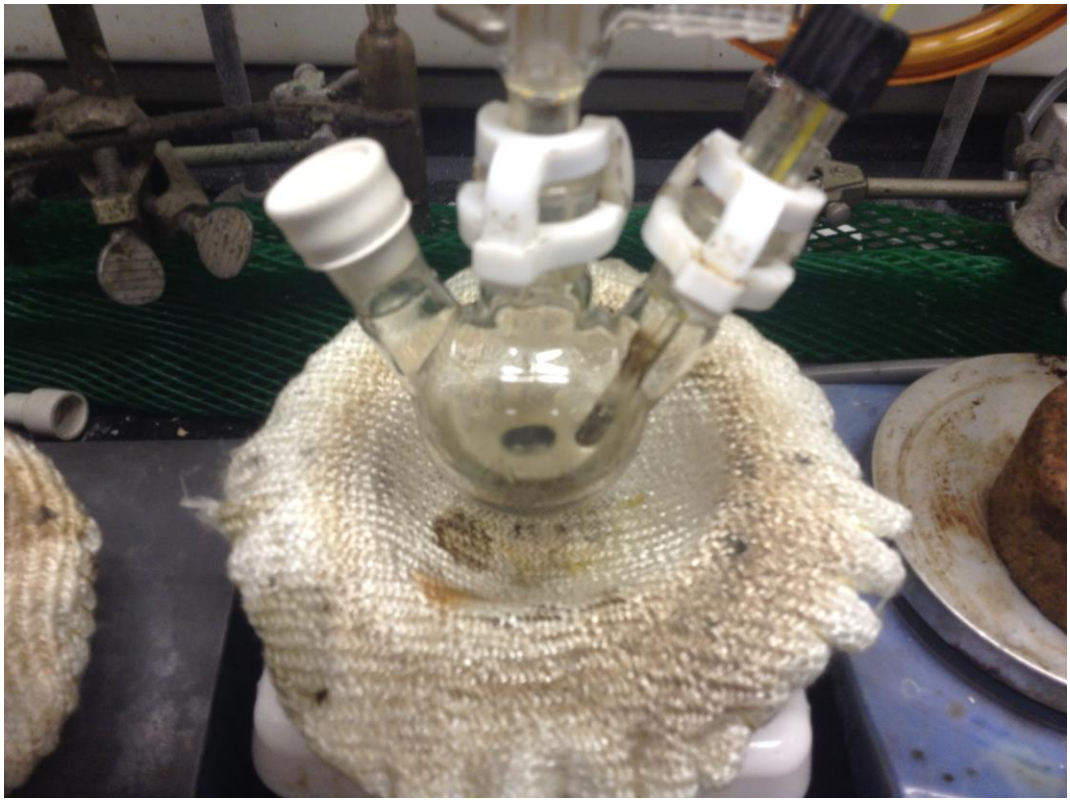
S.I. Figure 3. a) TEM of post annealed FeGa nanocomposites with elemental mapping on right. b) EDS spectrum obtained at purple marker point on composite map showing an elemental composition of $Fe_{37}Ga_{63}$. c) EDS spectrum obtained at yellow marker point on composite map having a elemental composition of $Fe_{83}Ga_{17}$.

S.I. Figure 3 displays TEM image of post annealed FeGa alloys. It can be seen that the amorphous particles have transformed into an agglomerate of smaller particles.

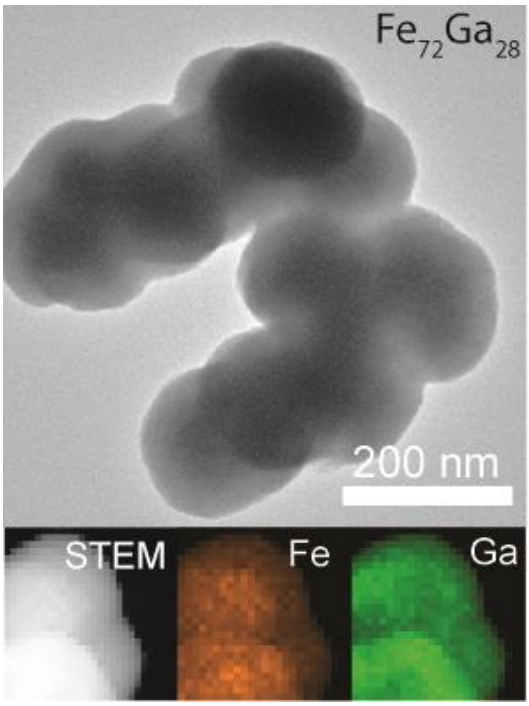
Elemental mapping shows that the final particles do not anneal into one phase, with two different regions within the nanocomposite. S.I. Figure 3b shows the EDS spectrum obtained on the purple marker, displaying higher gallium content, corresponding to the Fe_3Ga_4 phase in the XRD. S.I. Figure 3c shows EDS spectrum obtained at the yellow marker showing a higher iron content phase, corresponding to the α-Iron phase with gallium dissolved into it.



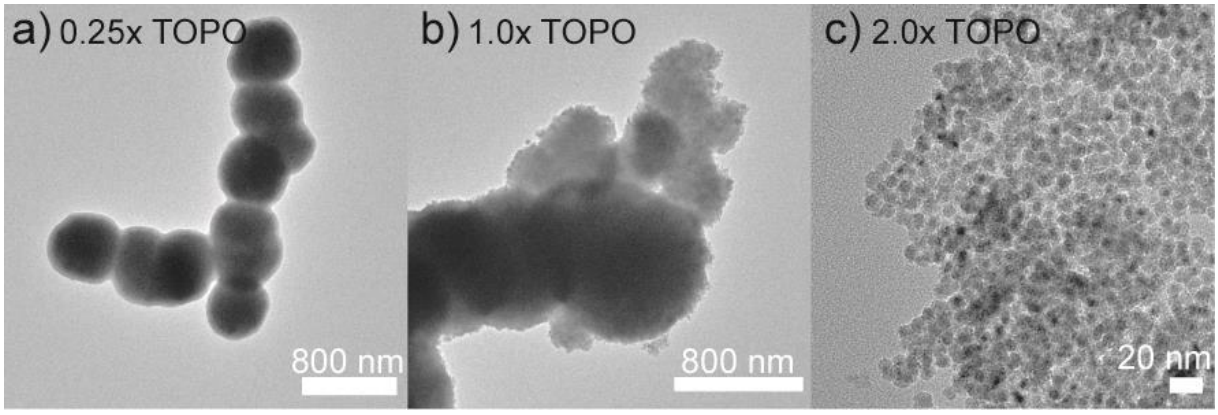
S.I. Figure 4. High Resolution TEM image showing annealed FeGa nanoalloys. α-Fe phase is outlined in red with lattice matching to {110} plane (JCP2 00-006-0696). Fe_3Ga_4 phase is outlined in white and two lattices visible match to the {004} and {420} planes (JCP2 01-071-0331).



S.I. Figure 5. Reaction vessel after reaction of $Ga(acac)_3$ and 2 molar equivalents of Oleylamine at 320 °C for 1 hour. White powder next to stir bar is unreacted $Ga(acac)_3$ and no visible color change occurs, indicating no reaction.



S.I. Figure 6. TEM image of FeGa nanoalloys produced with 0.25x molar amount of Oleylamine with elemental mapping below.



S.I. Figure 7. a) TEM image of FeGa nanoalloys with 0.25x molar amount TOPO. b) TEM image of FeGa nanoalloys produced with 1.0x molar amount TOPO. c) TEM of 2x TOPO at higher magnification to better show size.

At lower molar amounts of TOPO, the FeGa nanoalloys exhibit very similar structure to pristine FeGa nanoalloys. When TOPO molar amount is increased to 1x, aggregates of smaller FeGa particles appear with the large FeGa nanoalloys. By increasing to 2x TOPO molar amounts, only the smaller FeGa particles are produced.