Supplemental Information

The impact of carbon coating on the synthesis and properties of

Fe₁₆N₂ powders

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Figure S1. Rietveld analysis of passivated, carbon-coated Fe precursor. Data were collected using Cu K α radiation on a Scintag diffractometer. The data are fitted with a mixture of Fe (26.5(1)%; black), Magnetite Fe₃O₄ (19.5(2)%; red), Pnma Fe₃C (30.4(3)%; blue), and P6₃22 Fe₃C (23.5(5)%; green). A weak, broad peak appears to be present near ~51° that may be due to an additional carbide phase but cannot be conclusively identified.



Figure S2. Rietveld analysis of Fe_2O_3 nanoarc precursor. Data were collected using Mo K α radiation on a Bruker D8 advance. The sample is largely maghemite in space group P4₃32. A weak additional peak is present near to 12.79° that is suggests an additional phase on the order of a few percent or less. There is a report of tetragonal Fe_2O_3 with a tetragonal structure that would include this reflection, but a single weak peak is insufficient to provide conclusive identification. Furthermore, the reduced sample appears to be phase pure iron, which suggests the peak is associated with an iron oxide phase.



Figure S3. Rietveld analysis of (a) reduced Fe_2O_3 NanoArc, and (b) reduced carbon-coated Fe precursor. Data were collected using Mo K α radiation on a Bruker D8 diffractometer. The data are fitted with only an iron phase, and there is no evidence for other compounds. The reduction in (a) occurred at 400°C for 1.1 h under H₂, and for (b) was 400°C at 1h followed by 160°C for 21h under H₂. Excluded regions are present to remove the contribution from Mo K_{β} radiation that is not fully removed by the Zr filter. The difference is largely due to difficulties in fitting the effect of the spectrum produced by the Zr filter on the background, which results in an asymmetric shape beneath the peaks.



Figure S4. Rietveld analysis of sample FND (prepared from Fe₂O₃ precursor via reduction at 400°C for 1h under H₂ followed by 160°C for 21h under NH₃. Data were collected using Mo K α radiation on a Bruker D8 diffractometer. The data are fitted with a mixture of α ''-Fe₁₆N₂ (37.8(2)%; purple), Fe (50.1(1)%; red), Fe3O4 (6.4(1)%; blue), Fe4N (3.0(5)%; green) and Fe3N (2.7(3)%; black). The refined content of Fe₈N (α '-Fe₁₆N₂) was zero according to the available data.



Figure S5. Rietveld analysis of sample FNA (prepared from carbon coated Fe precursor via reduction at 400°C for 1h under H₂ followed by 160°C for 21h under NH₃. Data were collected using Cu K α radiation on a Scintag diffractometer. The data are fitted with a mixture of α ''-Fe₁₆N₂ (62.9(1)%; green), Fe (14.3(2)%; red), Fe₄N (3.0(3)%; blue) and Fe₃N (19.8(4)%; black). The refined content of Fe₈N (α '-Fe₁₆N₂) was zero according to the available data.



Figure S6. Rietveld analysis of sample FNB (XRD data are for one of two batches of carbon coated Fe precursor) prepared via reduction at 400°C for 1h under H₂ followed by 160°C for 21h under NH₃. Data were collected using Cu K α radiation on a Scintag diffractometer. The data are fitted with a mixture of α'' -Fe₁₆N₂ (58.9(5)%; green), Fe (20.6(6)%; red), Fe₄N (3.6(6)%; blue) and Fe₃N (17(1)%; black).



Figure S7. Rietveld analysis of sample FNB (neutron data are for two batches of carbon-coated Fe precursor) prepared via reduction at 400°C for 1h under H₂ followed by 160°C for 21h under NH₃. Data were collected using the POWGEN beamline at the SNS. The data are fitted with a mixture of α'' -Fe₁₆N₂ (51.1(5)%; green), Fe (15.1(3)%; red), Fe₄N (4.9(4)%; blue) and Fe₃N (29(1)%; black).



Figure S8. Rietveld analysis of sample FNC (four batches of carbon-coated Fe precursor) prepared via reduction at 400°C for 1h under H₂ followed by 160°C for 21h under NH₃. Data were collected using Mo K α radiation on a Bruker D8 diffractometer. The data are fitted with a mixture of α ^{''}-Fe₁₆N₂ (51.7(5)%; orange), Fe (21.0(4)%; red), Fe₄N (8.5(5)%; blue), Fe₃O₄ (3.4(4)%; green) and Fe₃N (15.4(5)%; black).



Figure S9. XPS analysis of the surface of precursor Fe-C powder, and that of sample FNC after reduction and ammonolysis.



Figure S10. XPS analysis of precursor Fe-C powder before and after Ar-ion sputtering. Core level spectra were taken on both the as received powder (red) and at the end of the Ar-ion depth profiles (green). The data are plotted in relative intensity to show the change in signal strength. The various portions of the data related to differing bonding arrangements (i.e. chemistry) are indicated. Sputtering clearly removes Fe_3O_4 and carbon coating to reveal Fe-Fe and Fe-C bonding.



Figure S11. XPS analysis of sample FNC powder before and after Ar-ion sputtering. Core level spectra were taken on both the as received powder (red) and at the end of the Ar-ion depth profiles (green). The data are plotted in relative intensity to show the change in signal strength. The various portions of the data related to differing bonding arrangements (i.e. chemistry) are indicated. Sputtering clearly removes Fe₃O₄ passivation layer, and reveals Fe-Fe and Fe-C bonding, as well as enhancing the Fe-N signal.



Figure S12. TEM characterization of a portion of one batch of sample FNC. Left: At lower temperatures ordering of the $Fe_{16}N_2$ lattice is evident. Right: After only 5 minutes at 200 °C the lattice ordering has essentially disappeared.



Figure S13. Left: Particles of α'' -Fe₁₆N₂ are spherical and appear to be single crystals or twinned crystals, coated with a C layer. These typically show only Fe. N is not detected due to self-absorption and there is no evidence for oxygen in these crystals. **Right**: A small fraction of the particles appear as irregularly shaped aggregates that typically exhibit substantial O peaks, suggesting FeO_x phase(s). This suggests that some poorly coated, aggregated particles in the commercial Fe-C powder are not fully converted during the reduction and ammonolysis. The possibility for particles that are not fully coated is suggested by the presence of magnetite Fe₃O₄ in the Fe-C precursor. To obtain pure α'' -Fe₁₆N₂ the particles should ideally be uniform in size, and more uniformly coated with carbon.