

Supplementary information

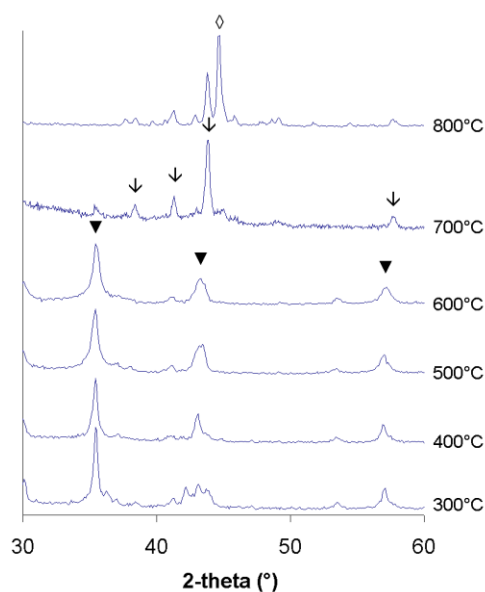


Figure S1 Full PXRD quenching profile for iron nitrate/gelatin calcined at 10 °C/min with labelled peaks corresponding to Fe_3O_4 ($\blacktriangledown$), Fe_3N ($\blacktriangledown$) and Fe ($\diamond$). The apparent peak broadening of the Fe_3O_4 possibly indicates the presence of the reduced phase FeO , as observed in other samples (e.g. Figure S2c). However, individual peaks cannot be resolved.

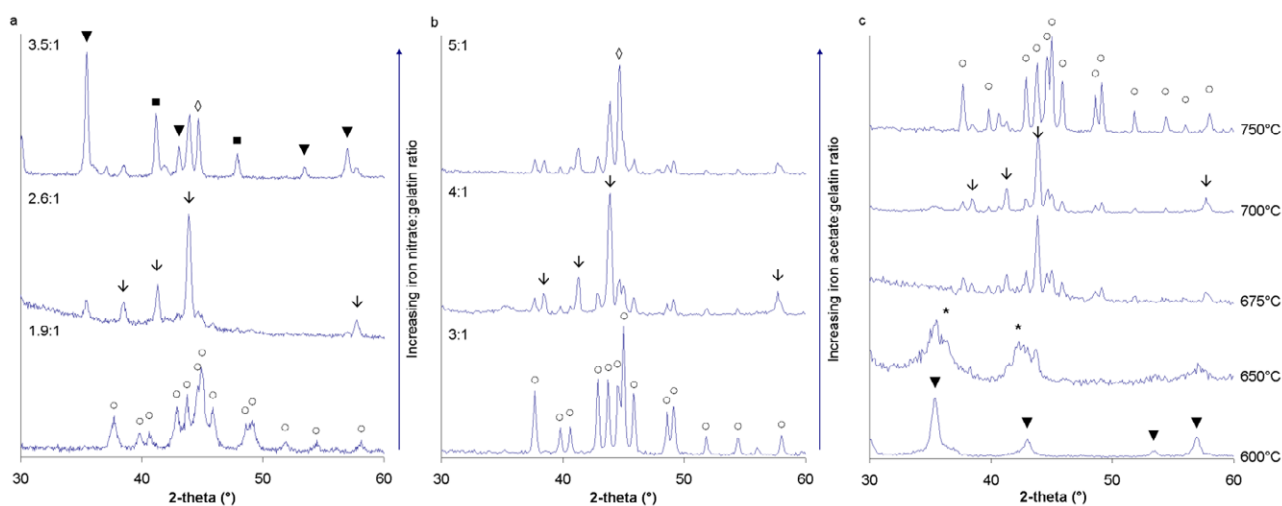


Figure S2 PXRD patterns for samples of (a) iron nitrate/gelatin and (b) iron acetate/gelatin at different metal:biopolymer ratios calcined at 10 °C/min to 700 °C. PXRD patterns for (c) samples of iron acetate/gelatin at a 4:1 mass ratio quenched at various temperatures during calcination at 10 °C/min under N_2 . Labelled peaks correspond to Fe_3O_4 ($\blacktriangledown$), FeO (*), Fe_3N ($\blacktriangledown$), Fe_4N ($\blacksquare$), Fe ($\diamond$) and Fe_3C ($\circ$). NB: additional small peaks have been left unlabelled but correspond to one of these crystalline phases.

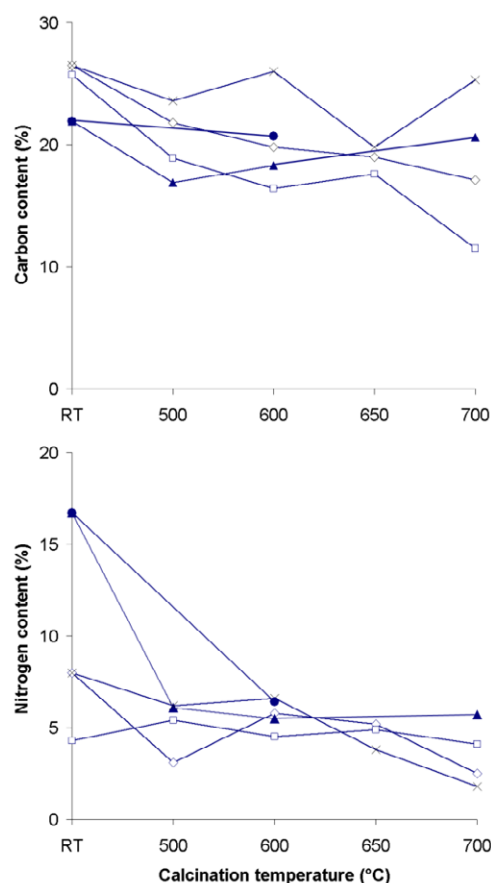


Figure S3 Percentage carbon and nitrogen content of samples quenched during calcination at 10 °C/min from iron nitrate/gelatin (▲) and iron acetate/gelatin 3:1 mass ratio (◇) and 4:1 mass ratio (□). Carbon and nitrogen content of samples calcined at 2 °C/min from iron nitrate/gelatin (●) and iron acetate/gelatin 3:1 mass ratio (×).

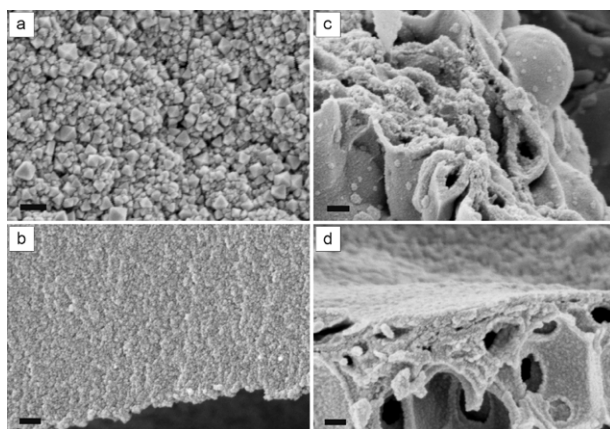


Figure S4 SEM images of samples quenched at 600 °C during synthesis from iron acetate at (a) 2 °C/min and (b) 10 °C/min and iron nitrate at (c) 2 °C/min (d) 10 °C/min. All scale bars = 200nm

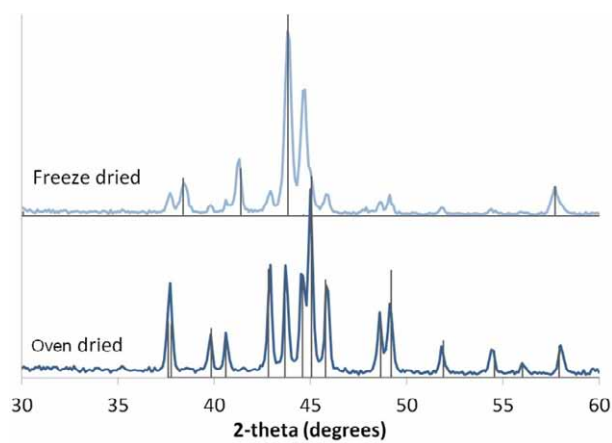


Figure S5 PXRD patterns of (a) freeze dried and (b) oven dried (dense film-like) samples of iron acetate/gelatin calcined to 700°C.

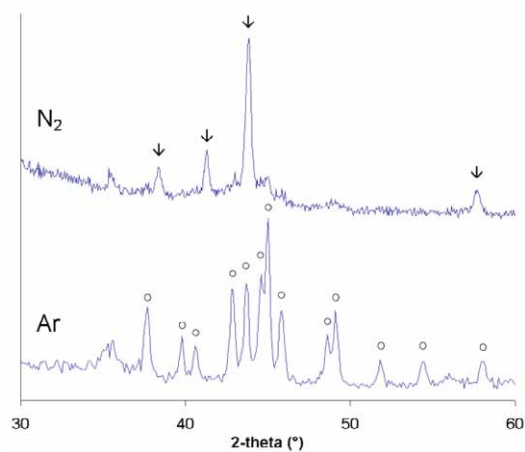


Figure S6 PXRD patterns for identical samples of iron nitrate/gelatin calcined at 10 °C/minute to 700 °C with no dwell under nitrogen and argon atmospheres. Labelled peaks correspond to Fe_3C (○) and Fe_3N (↓).

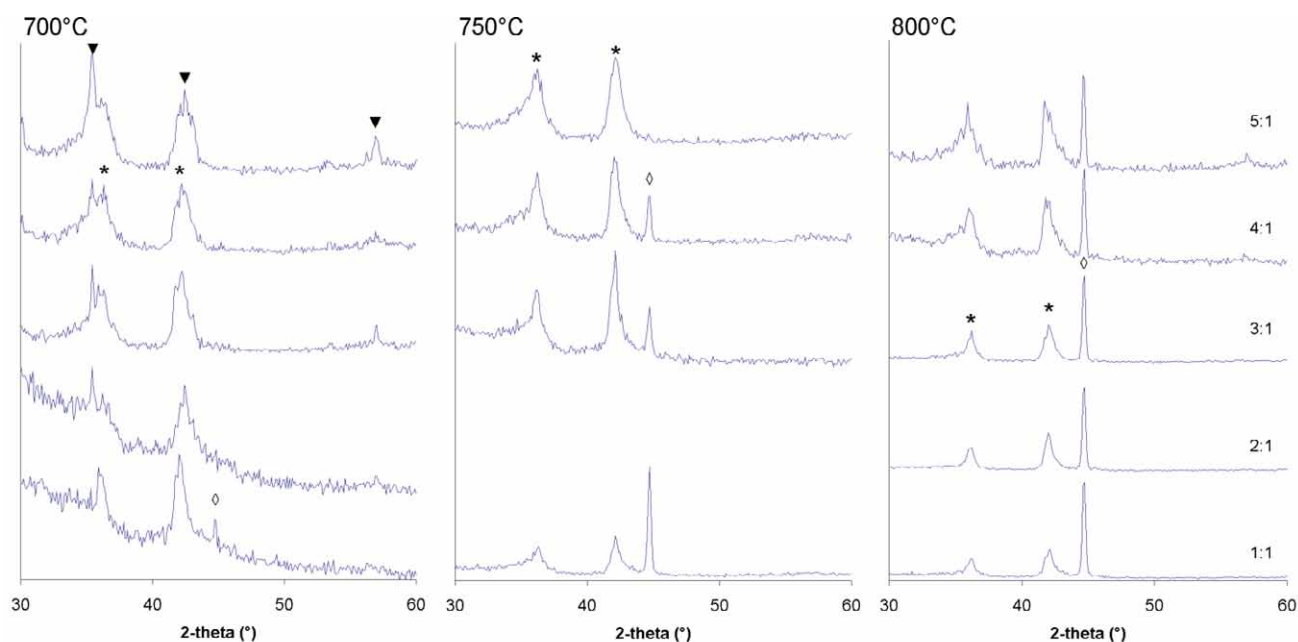


Figure S7 Samples of iron acetate/agar (mass ratio $\text{Fe}(\text{OAc})_2$:agar from 1:1 to 5:1) calcined at 10 °C/min under nitrogen to various temperatures with no dwell time. Labelled peaks correspond to Fe_3O_4 (▼), FeO (*) and Fe (◇).

Characterization Techniques

PXRD was carried out on a Bruker D8 Advance diffractometer (Copper K-alpha radiation) equipped with a LynxEye detector. Samples for scanning electron microscopy (SEM) were dispersed on carbon adhesive pads, coated with platinum/palladium and analyzed using a Field Emission JEOL JSM-7500F SEM. Transmission electron microscopy (TEM) images were taken on a Zeiss EM 912 Ω operated at an acceleration voltage of 120 kV. Samples were ground, suspended in ethanol and sonicated for 2 minutes in an ultrasonic bath. One drop of this suspension was put on carbon-coated copper grid and left in air to dry.

For catalytic testing, we used pure ammonia in a quartz tube reactor with inner and outer tube. The inner tube contains a quartz frit with a diameter of 5.5 mm on which the material is placed. The height of the material is between 2 and 5 mm and we used 25mg. The flow rate was 15000 $\text{cm}^3 \text{g}^{-1} \text{catalyst hr}^{-1}$.