Supporting Information

Microwave-Assisted Deep Eutectic-Solvothermal Preparation of Iron

Oxide Nanoparticles for Solar Water Splitting

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1) Raman Spectroscopy of prepared iron oxides

A small amount (~1 mg) of each prepared iron oxide was placed on a clean glass slide and measured for 30 seconds using a Renishaw inVia confocal Raman microscope with a 532 nm laser. All products showed similar scattering, likely due to the action of the laser light upon the samples, either oxidising or otherwise fusing nanoparticles to a crystalline α -Fe₂O₃ form.



Figure ESI-1. Raman spectra for the prepared iron oxide samples. Data are smoothed and corrected for cosmic radiation.

2) Residual mass within the autoclaves

The nanoparticle-forming reactions performed using the iron precursors were found to form a white crystalline crust around the top of the vessel. This was carefully removed from the autoclave used for the Fe-200-0 synthesis for testing. Samples were measured using ¹H NMR. Numerous deuterated solvents were tried (acetone, acetonitrile, chloroform, methanol, ethanol) but the product was only soluble in D₂O. This suggests that the product likely contains a highly polar, ionic species such as the anticipated ammonium carbonate. The ¹H NMR spectrum of this product is shown in Figure ESI-2.



Figure ESI-2. ¹H NMR spectrum of the Fe-200-0 reactor residue collected using a 500 MHz Agilent ProPulse NMR Spectrometer. The solute was dissolved in D_2O . The inset shows a zoomed region $\sim 2 - 4$ ppm.

Analysis of the products with powder X-Ray diffraction revealed strong scattering corresponding with a highly crystalline material, shown in Figure ESI-3. Because of the unknown composition of the material, indexing was not attempted.



Figure ESI-3. Powder X-Ray diffraction data for the residual crystalline product formed at the roof of the reactor for the high-temperature, low-water reaction.

3) Heat treatment experiments on Deep Eutectic Solvents

¹H NMR spectra for the heat treated DESs are shown in Figures ESI-4 to ESI-9. Data were collected using an Agilent ProPulse 500 MHz NMR spectrometer. Samples (~20 mg) were diluted into d_6 -DMSO (~0.6 g). Integrals are shown below the peaks and the centre position shown above. The choline –(CH₃)₃ feature was used universally as a reference integral.



Figure ESI-4. ¹H NMR spectrum of the 0w DES treated at 100 °C for 10 minutes.



Figure ESI-5. ¹H NMR spectrum of the 0*w* DES treated at 150 °C for 10 minutes.



Figure ESI-6. ¹H NMR spectrum of the 0*w* DES treated at 200 °C for 10 minutes.



Figure ESI-7. ¹H NMR spectrum of the 10*w* DES treated at 100 °C for 10 minutes.



Figure ESI-8. ¹H NMR spectrum of the 10w DES treated at 150 °C for 10 minutes.



Figure ESI-9. ¹H NMR spectrum of the 10w DES treated at 200 °C for 10 minutes.

4) Front and back illumination comparison for photoanodes

It was typically found that 'back illumination', that is, the illumination of the uncoated side of the FTO glass slide, gave far higher photocurrent densities than illuminating the coated side of the sample. This is related to the thickness and porosity of the electrode; assuming that the highly porous nature of our films allows the entire surface are of the nanostructures to be wetted by the electrolyte solution, back illumination gives the highest photocurrent because more photoinduced electrodes are produced closer to the FTO substrate, and more electrons are therefore able to move to the cathode, with holes able to reach the liquid independent of this distance because of the film porosity. Additionally, light intensity scales negatively with film thickness due to absorption effects. An example of performance for front versus back illumination is shown in the following figure.



Figure ESI-10. The difference between front and back illumination for the Fe-150-10 film product is shown. The front illumination current is nearly imperceptible in comparison. Data were collected whilst chopping the shutter on and off with 0.5 s^{-1} periodicity.