

Electronic Supplementary Information (Eight pages)

Greener synthesis of nanofibrillated cellulose using magnetically separable TEMPO nanocatalyst

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Chemicals

Iron (II) chloride tetrahydrate (FeCl₂ · 4H₂O), sodium hypochlorite solution (NaClO with 10-15% available chlorine), tetraethyl orthosilicate (C₈H₂₀O₄Si, TEOS), (3-Aminopropyl) triethoxysilane (H₂N(CH₂)₃Si(OC₂H₅)₃, APTS), 4-Oxo-2,2,6,6-tetramethyl-1-piperidinyloxy (C₉H₁₆NO₂, 4-Oxo-TEMPO), 5-Ethyl-2-methylpyridine borane complex (C₈H₁₄BN), hydrochloric acid (HCl, 37%) ammonium hydroxide (NH₄OH, 28-30% NH₃ basis), toluene (C₆H₅CH₃, anhydrous 99.8%), ethanol (C₂H₅OH, anhydrous) were procured from Sigma-Aldrich Canada Co., Oakville, Ontario. Iron (III) chloride (FeCl₃, anhydrous), sodium bromide (NaBr) and sodium hydroxide (NaOH) were procured from Fischer Scientific Company, Ottawa, Canada. All the procured chemicals were ACS reagent grade. Distilled water was produced in laboratory using Barnstead Mega Pure system.

Characterization of Fe@MagTEMPO and nanofibrillated cellulose

Scanning electron microscopy (SEM) images were captured with Hitachi S3000N VP SEM with energy dispersive X-ray spectroscopy (EDX). 0.1% (w/w) suspension of nano fibrillated cellulose was dried overnight in vacuum oven at 40° C to make a film. The film was loaded on SEM sample stub and sputter coated with gold to prevent charring during analysis. Transmission electron microscopy (TEM) images were captured with Hitachi H7600 TEM equipped with AMT XR50 CCD camera. 20 mg catalyst sample was dispersed in ethanol and few drops of suspension were put on 400-mesh, 3.5 mm copper grid. Fourier transform infrared spectroscopy (FTIR) was done with Perkin Elmer Spectrum One system to investigate the stability of catalyst under oxidation conditions. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra of nanofibrillated cellulose films made using homogeneous TEMPO and Fe@MagTEMPO catalysts were recorded using Pike Miracle ATR accessory with diamond crystal. Atomic force microscopy (AFM) images were captured using Veeco multimode 8 system and RTESPA-150 cantilever tip with force constant of 5 N.m⁻¹ and resonant frequency of 150 kHz. A drop of 0.001% (w/w) suspension of nanofibrillated cellulose in water was put on freshly cleaved mica sheet and dried in vacuum at 40° C before AFM analysis. UV-Visible spectroscopy analysis was done using Varian Cary 50 Bio spectrophotometer.

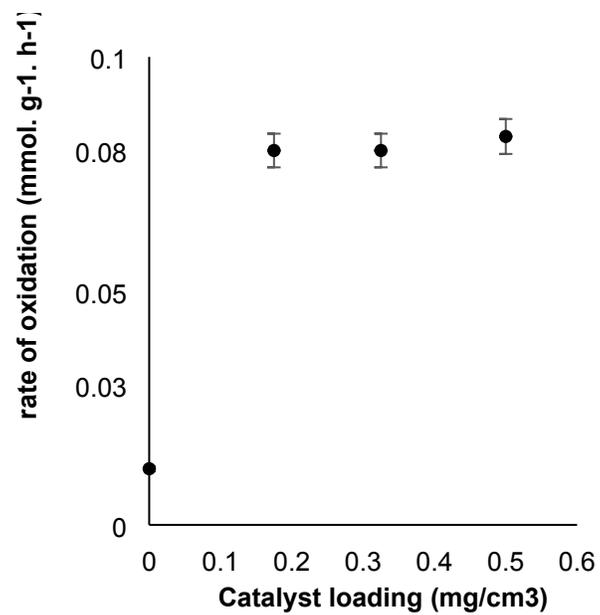


Figure ES1: Effect of catalyst loading on rate of oxidation of cellulose pulp

2 g never dried bleached softwood pulp, 200 cm³ water, 0.1 mmol NaBr, 5 mmol/g NaClO, NaOH (0.5M) to maintain pH 10,
T= 25° C

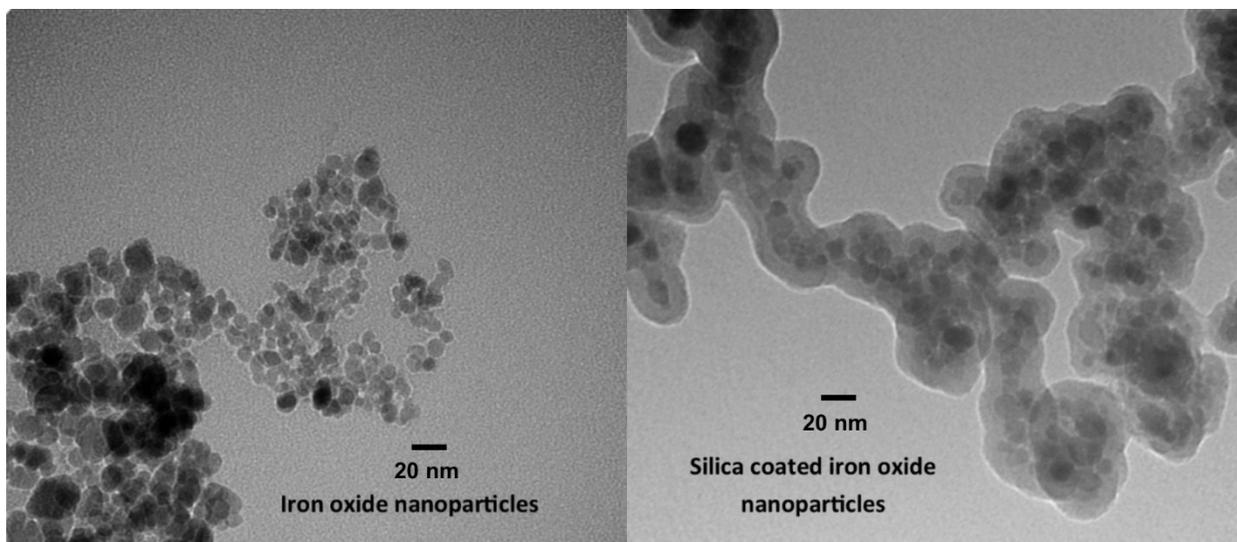


Figure ES2: TEM images of iron oxide nanoparticles and silica coated iron oxide nanoparticles

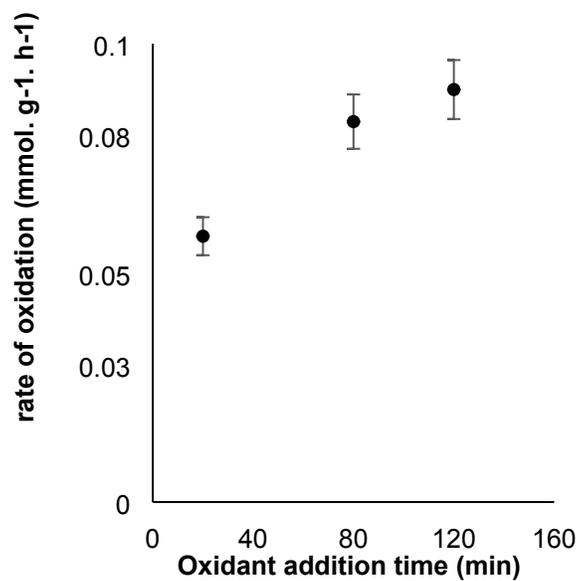


Figure ES3: Effect of oxidant addition time on rate of oxidation of cellulose pulp

2 g never dried bleached softwood pulp, 200 cm³ water, 0.1 mmol NaBr, 0.175 mg/cm³ Fe@MagTEMPO, 5 mmol/g NaClO, NaOH (0.5M) to maintain pH 10, T= 25° C

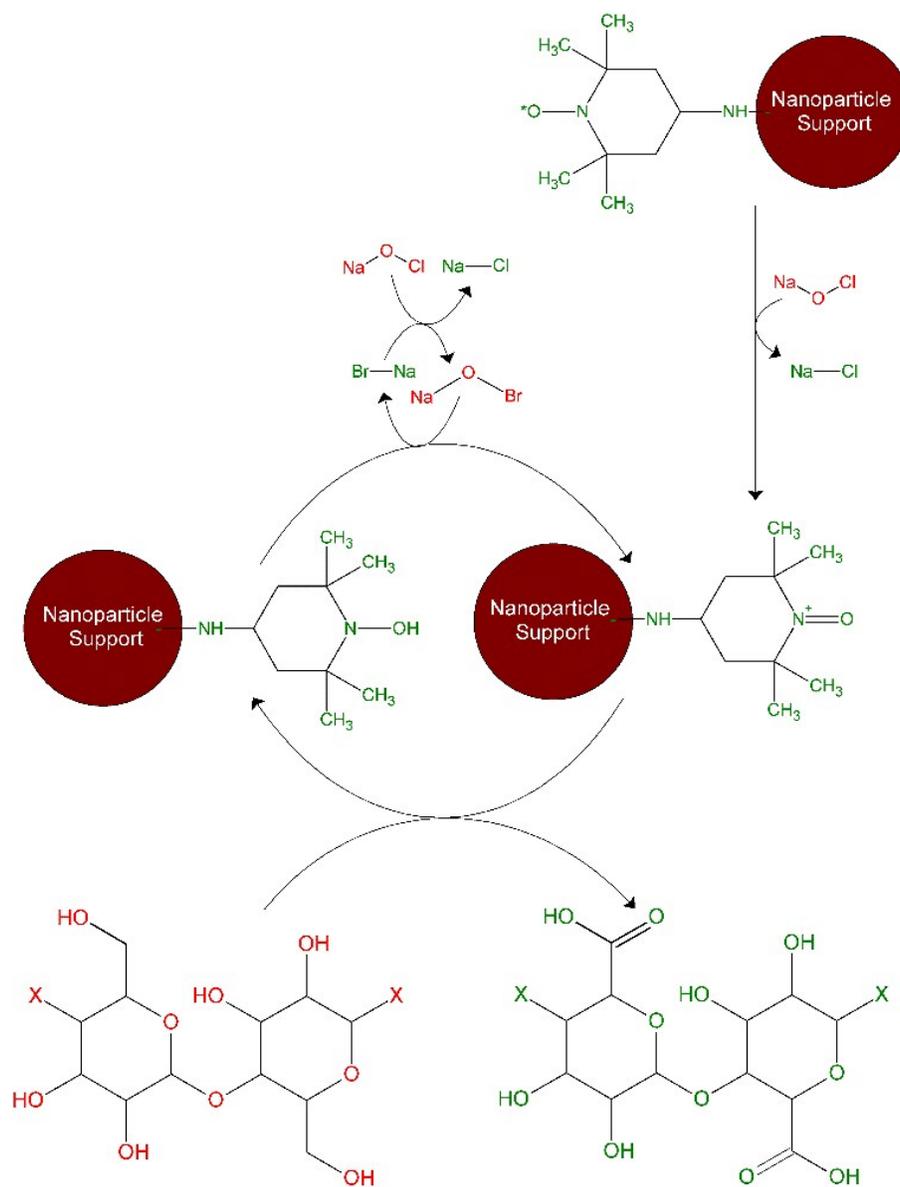


Figure ES4: Oxidation of C-6 primary hydroxyls with Fe@MagTEMPO

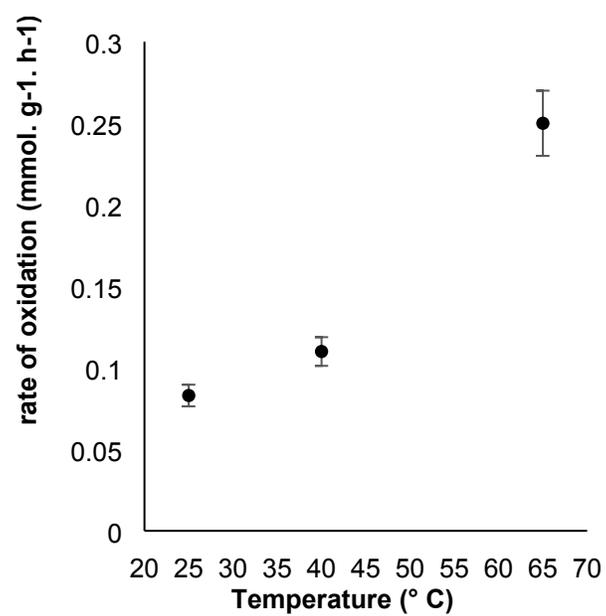


Figure ES5: Effect of temperature on rate of oxidation of cellulose pulp

2 g never dried bleached softwood pulp, 200 cm³ water, 0.1 mmol NaBr, 0.175 mg/cm³ Fe@MagTEMPO, 5 mmol/g NaClO, NaOH (0.5M) to maintain pH 10

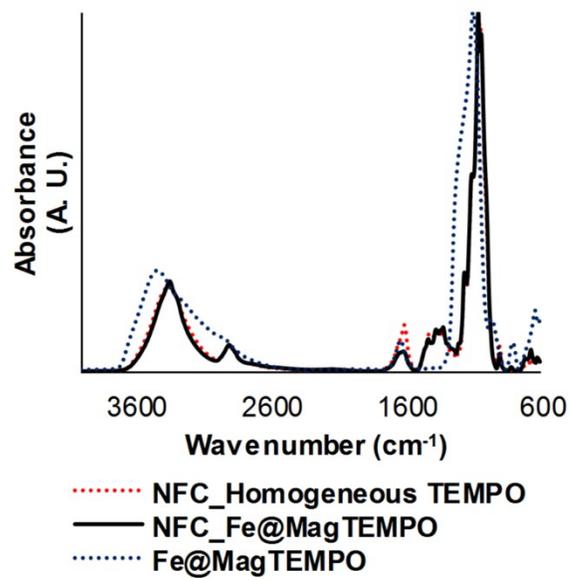


Figure ES6: ATR-FTIR analysis of nanofibrillated cellulose films made from homogeneous TEMPO and Fe@MagTEMPO catalysts

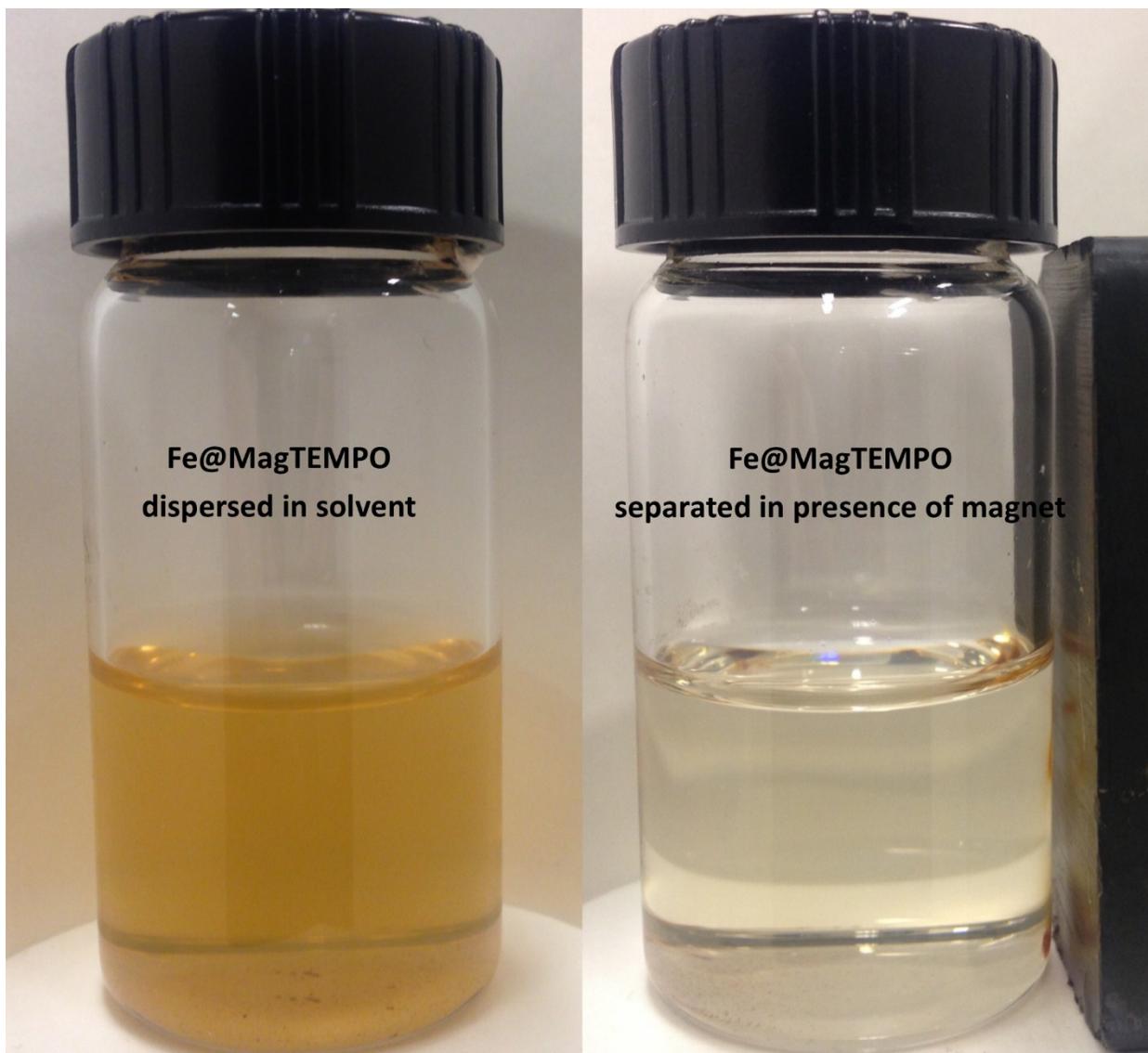


Figure ES7: Dispersion of Fe@MagTEMPO in solvent and separation in presence of magnetic force