Supplementary Information for:

Reversing aggregation: Direct synthesis of nanocatalysts from bulk metal. Cellulose nanocrystals as active support to access efficient hydrogenation silver nanocatalysts

Madhu Kaushik, Alain You Li, Reuben Hudson, Mitra Masnadi, Chao-Jun Li, and Audrey Moores*

Centre for Green Chemistry and Catalysis, Department of Chemistry, McGill University, 801 Sherbrooke St.West, Montréal, QC, H3A 0B8, Canada

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Materials and methods

Freeze-dried CNCs synthesised by sulphuric acid hydrolysis of wood pulp were provided by FPInnovations. The size of CNCs used were about 250 ± 80 nm in length and 8 ± 5 nm in width, with a sulphate ester coverage of 5-7%.[1] To redisperse dried CNC samples in suspension, the Sonics & Materials Inc. Vibra-Cell VC1500 ultrasonicator (220V, 15A, 1500W, 20 kHz) was used. The Metrohm Titrando (836 base, 804 Ti stand, and 802 stirrer) autotitrator was used for attaining various pH values. The transmission electron microscopy (TEM) samples were deposited on 400 mesh carbon coated copper grids supplied by Electron Microscopy Sciences. The analyses were performed on the Tecnai 12 microscope (FEI electron optics) equipped with a Lab6 filament at 120kV, equipped with Gatan 792 Bioscan 1k x 1k Wide Angle Multiscan CCD Camera (Gatan Inc.); and FEI G2 F20 Cryo-S/TEM microscope (FEI, Inc) at 200kV, equipped with Gatan Ultrascan 4k x 4k Digital (CCD) Camera System at different magnifications corresponding to different pixel size (defocus level ranging from − 2.5 to − 4.5 μm). ICP measurements were taken using a PerkinElmer NexIon® 350 ICP-MS to measure Ag content at the elemental wavelength of 328.068nm. XPS was performed on a VG ESCALAB 3 MKII spectrometer (VG, Thermo Electron Corporation, UK) equipped with an Mg Kα source. All hydrogenation reactions were carried out in a Parr Instruments 5000 Series Multiple Reactor System. The monitoring of catalytic hydrogenation was performed using an Agilent 7890A series gas chromatograph equipped with a MS detector (5975C) on an Agilent DB-WAX column and Agilent Cyclodex-B column. Cyclohexanol (reagentplus grade, 99%, Sigma Aldrich) was used as internal standard for quantification of all hydrogenation reactions. All reagents, solvents and substrates were procured from Sigma Aldrich.

Synthesis of AgNPs@CNCs

500 mg of CNCs were redispersed in 100 ml water. Ag wire (7 g, 2.0 mm diameter, 1.25 inches length) was added to the CNC suspension and stirred at room temperature for 20 days (Fig. S1). For blank comparisons, a silver wire was also immersed in water at stirred at room temperature for 20 days. The Ag content was monitored by ICP-MS. The resulting solution was drying by evaporation and the resulting AgNPs@CNCs was collected as a very light brown powder and fully characterized by XPS, TEM and EDAX experiments.

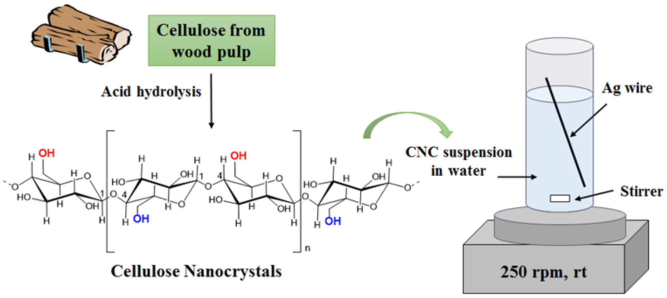


Fig. S1 Molecular structure of CNCs and the experimental set-up

Control experiments

<u>Absence of air:</u> 500 mg of CNCs were redispersed in 100 ml degassed water in glovebox. Ag wire (7 g, 2.0 mm diameter, 1.25 inches length) was added to the CNC suspension and stirred at room temperature for 15 days in absence of air (inside a glovebox). Samples for ICP measurements were taken at day 3, 7, 10 and 15.

Use of $AgNO_3$ as precursor: 500 mg of CNCs were redispersed in 100 ml $AgNO_3$ solution of water. The concentration of $AgNO_3$ in the system was 175 μg/L. The reaction was stirred at room temperature for 20 days and then used for the catalysis of hydrogenation of benzaldehyde.

ICP measurements

1 ml sample was taken out form the 100 ml CNC suspension being stirred at room temperature with Ag wire at day 3, 7, 10, 15 and 20. The liquid sample was then evaporated overnight in a vacuum oven and the residue was digested in 1mL of concentrated HNO_3. 0.25mL of the HNO_3 solution was then diluted using deionized water up to 25mL and the sample was tested using ICP-MS.

For leaching measurements, the product of benzaldehyde reduction is extracted after catalysis and put under vacuum to obtain a dry residue. This was digested in 1mL of concentrated HNO_3. 0.25mL of the HNO_3 solution was then diluted using deionized water up to 25mL and the sample was tested using ICP-MS. The concentration of Ag obtained by this measurement is based on 1 ml of HNO_3 solution. It is then divided by 5 to give the amount of Ag leached in reference to the 5mL of catalytic suspension used in this process. This allows a direct comparison of the Ag leaching amount with the Ag contained in the 5mL of the catalytic suspension.

TEM and EDS

5ul of samples were deposited on carbon film coated 200 Mesh copper EM grids for two minute, followed by blotting off the excess liquid with the edge of a filter paper. The grids were then imaged using FEI G2 F20 Cryo-STEM operated at 200 kV (FEI, Inc). Images were recorded with a Gatan Ultrascan 4k × 4k Digital (CCD) Camera System.

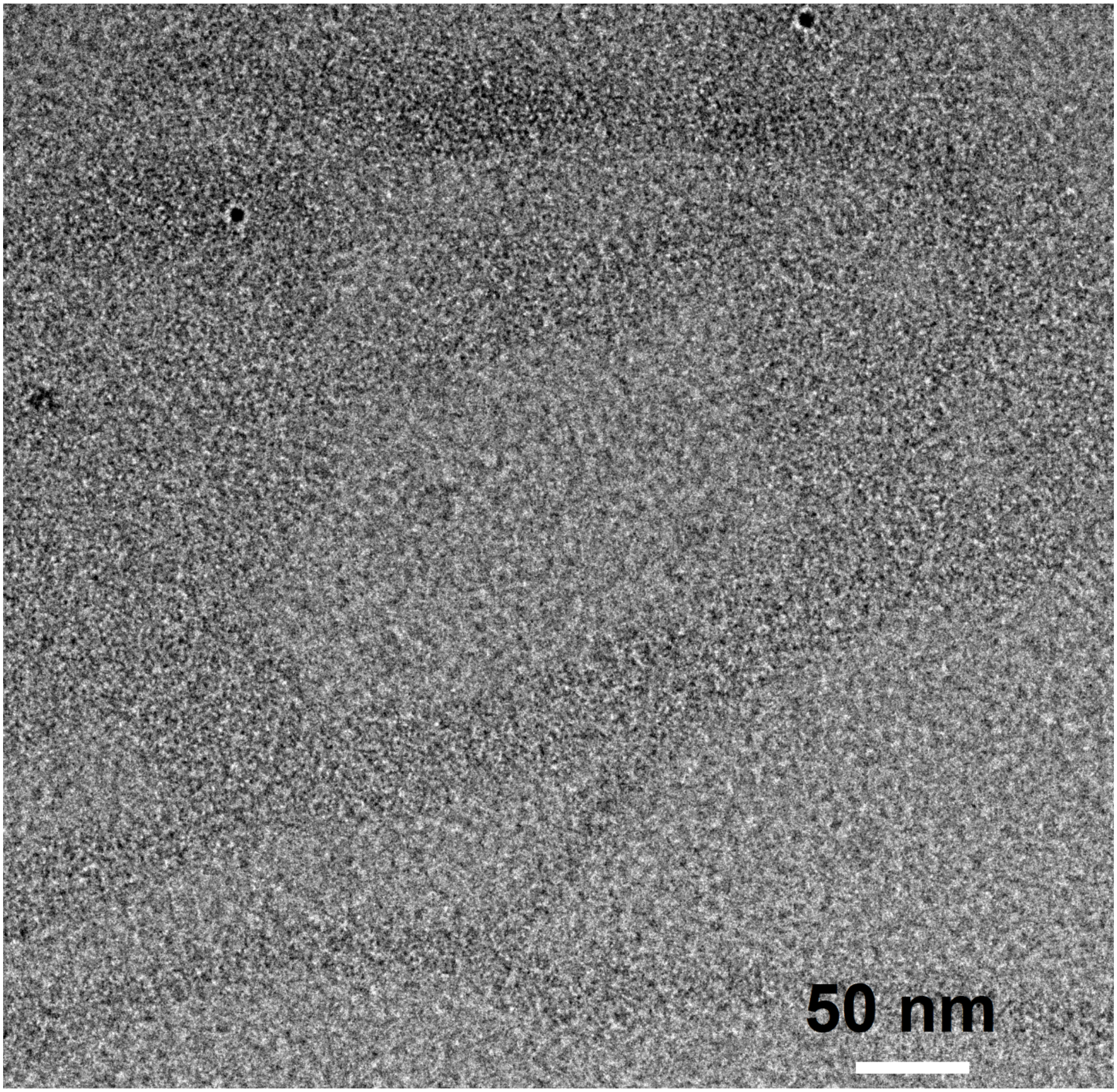


Figure S2: TEM of AgNPs@CNCs

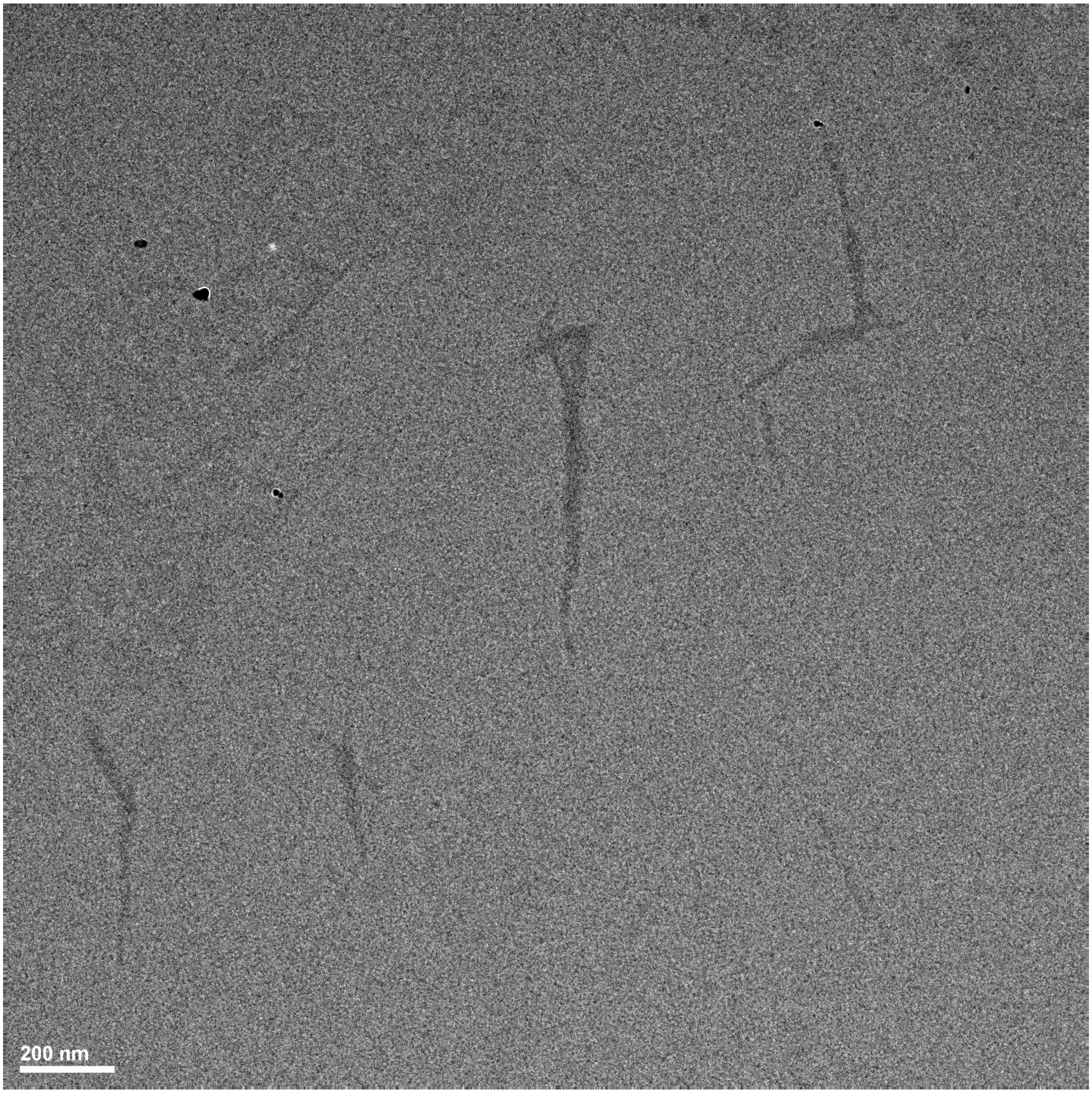


Figure S3: TEM of AgNPs@CNCs

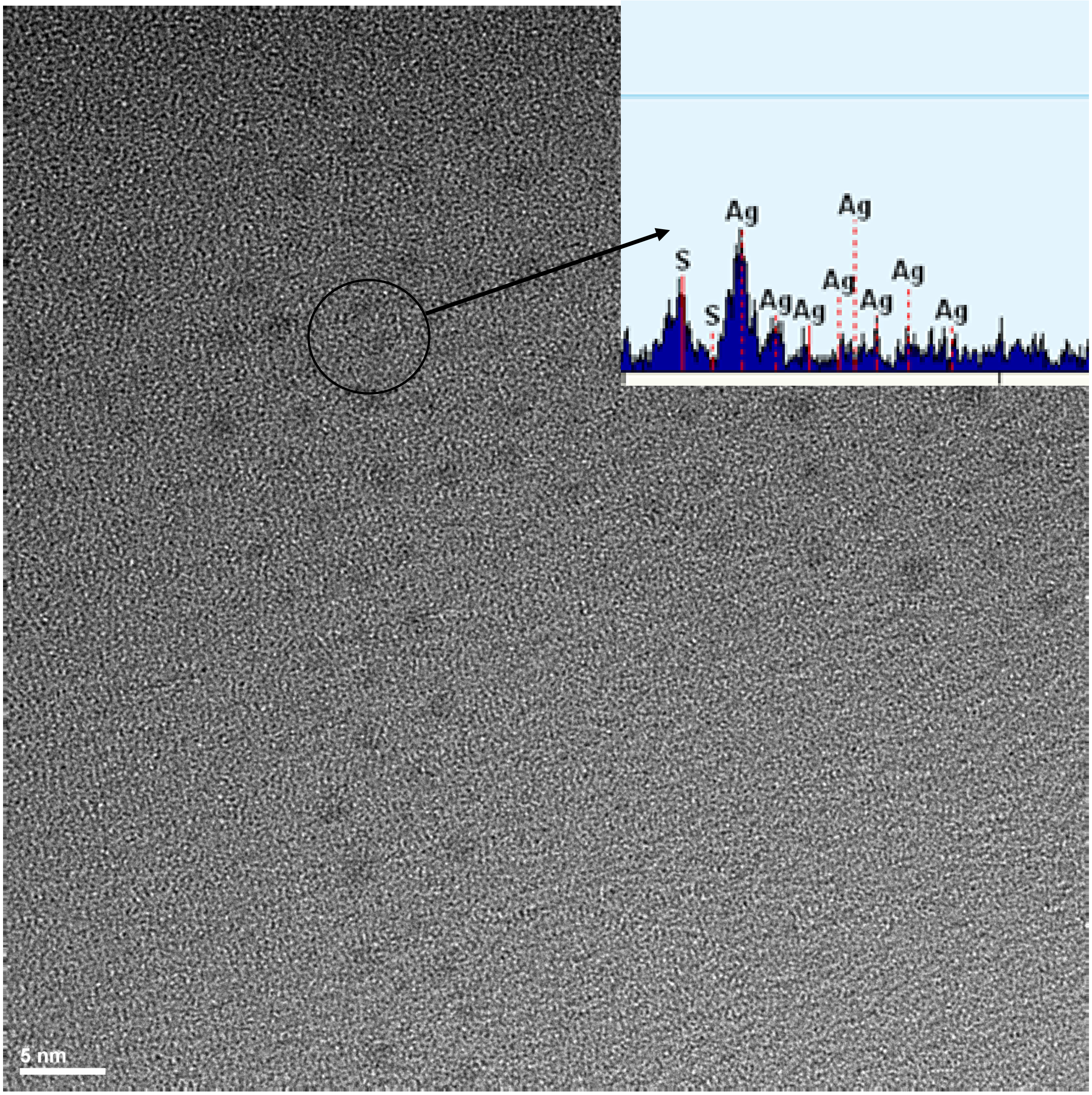


Figure S4: TEM of AgNPs@CNCs at higher magnification. The inset (top, right) shows the EDS, confirming the presence of Ag.

XPS study

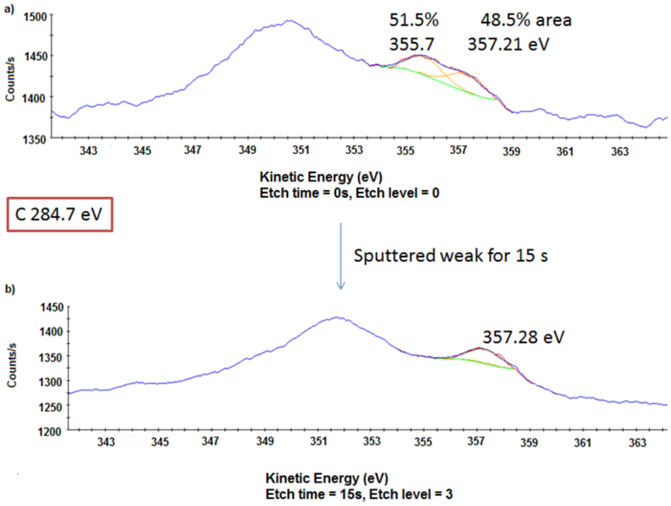
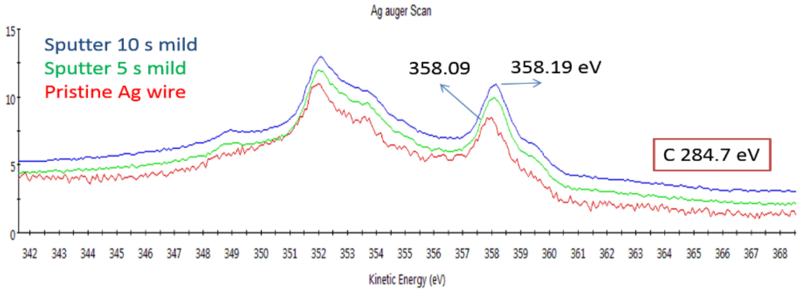


Figure S5: XPS spectrum in the Ag Auger region: a) AgNPs@CNCs, b) after sputtering an

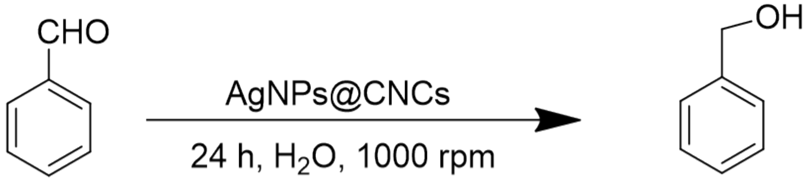


AgNPs@CNCs sample for 15 s.

Figure S6: XPS spectrum in the Ag Auger region of an Ag wire used as an Ag metal standard f

Optimization of pressure and temperature for hydrogenation reaction

In a typical reaction, substrate (0.1 mmol) was added to the catalyst suspension prepared above, AgNPs@CNCs, (5mL). To this mixture was added cyclohexanol (0.1 mmol) as internal standard. Then, the mixture was placed in a PARR multiple reactor system under various H_2 pressures and temperatures, 1000rpm, for 24 h (Table S1). Afterwards, the reaction mixture was extracted with diethyl ether and then injected on the GC-MS for monitoring the reaction.



Pressure (H_2)	Temperature (°C)	Conversion
20 bars	100	30 %
	150	33 %
30 bars	100	34 %
30 bars	125	45 %
40 bars	80	25 %
40 bars	100	96%

Table S1: Optimization of pressure and temperature for hydrogenation reaction

Hydrogenation of substrates

In a typical reaction, substrate (0.1 mmol) was added to the catalyst suspension prepared above, AgNPs@CNCs, (5mL). To this mixture was added cyclohexanol (0.1 mmol) as internal standard. Then, the mixture was placed in a PARR multiple reactor system under H_2 pressure, 40 bars, 1000rpm, for 24 h at 100°C. Afterwards, the reaction mixture was extracted with diethyl ether and then injected on the GC-MS for monitoring the reaction.

Monitoring the Hydrogenation Reactions

The monitoring of catalytic hydrogenation and determination of enantiomeric excess were performed using an Agilent 7890A series gas chromatograph equipped with a MS detector (5975C) on an Agilent Cyclodex-B column. Response factors for all compounds were calculated using cyclohexanol as the internal standard. The response factor was calculated by running a standard solution containing known substrate and internal standard concentrations on the GC-MS to determine the area of the two compounds:

Response Factor, R = (concentration of substrate/ concentration of internal standard)*(peak area of internal standard/ peak area of substrate)

Recycling experiments

Benzaldehyde (0.1 mmol) was added to the catalyst suspension prepared above, AgNPs@CNCs, (5mL). To this mixture was added cyclohexanol (0.1 mmol) as internal standard. Then, the mixture was placed in a PARR multiple reactor system under H_2 pressure, 40 bars, 1000rpm, for 24 h at 100°C. Afterwards, reaction mixture was extracted with diethyl ether and then injected on the GC-MS for monitoring the conversion. The remaining water suspension, having the catalyst, was then used for the next cycle. The process was repeated upto five cycles (figure S5). The conversion was good for 4 cycles, after which the catalyst gave only 12 % yield in the 5th cycle.

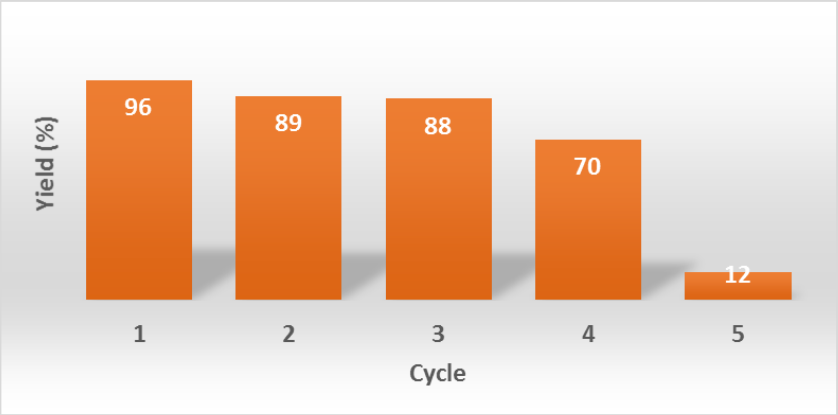
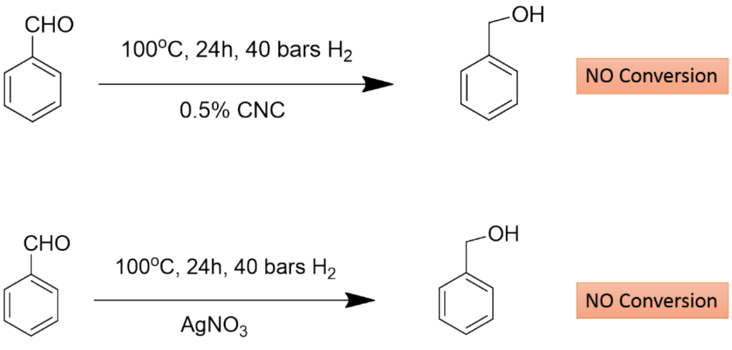


Fig. S7: Recycling Experiments

Control experiments for catalysis

Two types of blank experiments were conducted for benzaldehyde reduction under exactly similar conditions of temperature, pressure, Ag loading and no. of equivalents used for the substrate and catalyst. The CNCs alone were not active. In the second experiment, $AgNO_3$ was used in the absence of CNCs resulting in 0% conversion.



Concentration of Ag ion in reaction: 175 ug/L

Fig. S8: Control Experiments

1. a) M. Kaushik, W. C. Chen, T. G. M. van de Ven and A. Moores, *Nord. Pulp Pap. Res. J.*, 2014, 29, 77-84; b) M. Kaushik, C. Fraschini, G. Chauve, J.-L. Putaux and A. Moores, in *The Transmission Electron Microscopy*, ed. K. Maaz, InTech, 2015, p. DOI: 10.5772/60985.