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Supplementary Information for:

Cellulose nanocrystals as non-innocent support to the synthesis of ruthenium nanoparticles and their application to arene hydrogenation

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MATERIALS AND METHODS

CNCs synthesised by sulphuric acid hydrolysis of wood pulp were provided by FPInnovations. $RuCl_3.3H_2O$ was purchased from Pressure Chemicals. For the manipulation of pH, hydrochloric acid (0.01M) was provided by Fluka Analytical. 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 200 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). All hydrogenation reactions were carried out in a Parr Instruments 5000 Series Multiple Reactor System. 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 a 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 the catalyst, RuNPs@CNCs

100 mg of CNCs were weighed out in a 5-dram vial, to which 20 mL of deionised water was added to achieve a 0.5 wt% CNC solution. To this solution, 2.6 mg of $RuCl_3.3H_2O$ was added, affording a 63ppm solution in Ru. This solution was then sonicated for 10 seconds in order to completely dissolve the $RuCl_3.3H_2O$ in the water giving a very dark brown solution. After that the reaction mixture was mounted onto the Parr system for 24 hours at room temperature, 4 bars H_2 and 1000 rpm. The resulting suspension of the catalyst, RuNPs@CNCs, was black.

Control Experiments for synthesis of catalyst

Control 1: 100 mg of CNCs were weighed out in a 5-dram vial, to which 20 mL of deionised water was added. To this solution, 2.6 mg of $RuCl_3.3H_2O$ was added. This solution was then sonicated for 10 seconds in order to completely dissolve the $RuCl_3.3H_2O$ in the water giving a very dark brown solution. Then, NaBH4 (25 mg) was added and the reaction mixture was stirred at room temperature for 24 hours (Figure S1).

Control 2: 100 mg of CNCs were weighed out in a 5-dram vial, to which 20 mL of deionised water was added. To this solution, 2.6 mg of $RuCl_3.3H_2O$ was added. This solution was then sonicated for 10 seconds in order to completely dissolve the $RuCl_3.3H_2O$ in the water giving a very dark brown solution. The reaction mixture was stirred at room temperature for 24 hours, without adding any external reducing agent (Figure S1).

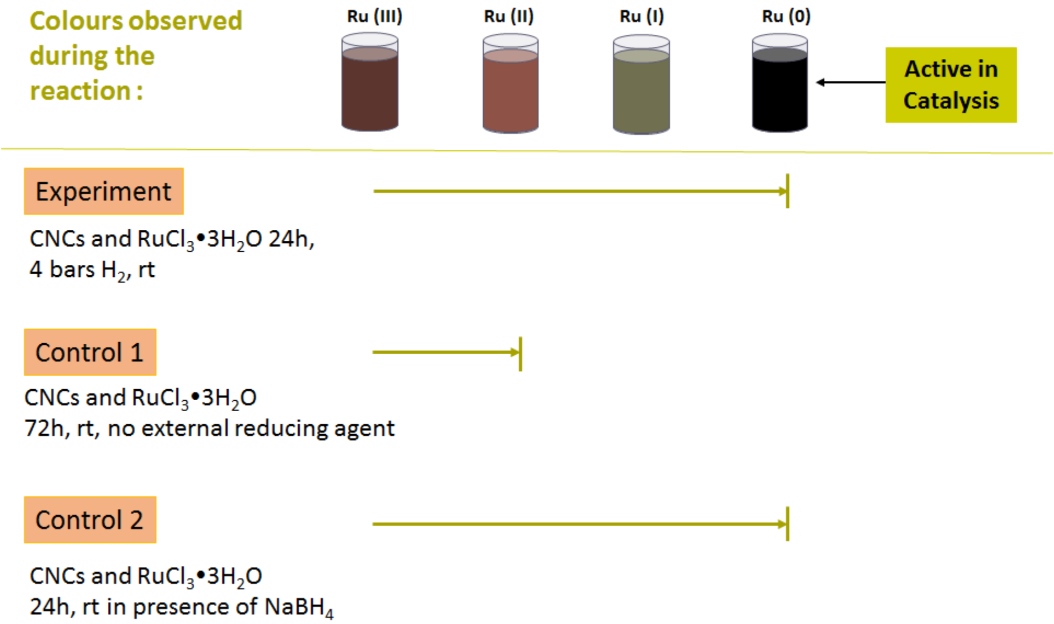

Figure S1: The colours observed during the experiments and the controls.

Monitoring the Hydrogenation Reactions

The monitoring of catalytic hydrogenation was 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).

Optimisation of reaction conditions for arene hydrogenation

Substrate (0.1 mmol) was added to the catalyst suspension prepared above, RuNPs@CNCs, (5mL). To this mixture was added cyclohexanol (0.1 mmol) as internal standard. Then, the mixture was mounted onto a PARR multiple reactor system under various conditions (Table 1 in the manuscript). For time optimization, the reaction was set to 20 bars, rt for 24h. Aliquots of 0.5 ml from the reaction mixture were then analyzed on GC-MS, at time 2h, 4h, 8h and 24h.

Hydrogenation of Substrates

Substrate (0.1 mmol) was added to the catalyst suspension prepared above, RuNPs@CNCs, (5mL). To this mixture was added cyclohexanol (0.1 mmol) as internal standard. Then, the mixture was mounted onto a PARR multiple reactor system under H_2 pressure, 4 bars, 1000rpm, for 24 h at room temperature (optimized conditions). Afterwards, reaction mixture was extracted with diethyl ether and then injected on the GC-MS for monitoring the conversion.

Recycling Experiments

Substrate (0.1 mmol) was added to the catalyst suspension prepared above, RuNPs@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, 4 bars, 1000rpm, for 24h at room temperature. 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 seven cycles (Figure S2).

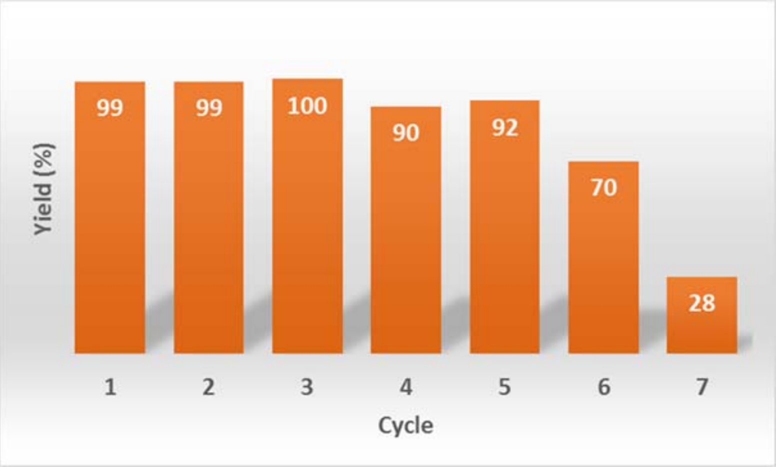

Figure S2: Recycling of toluene hydrogenation at 4bars H_2, rt, 24h

Poisoning Experiments

Substrate (0.1 mmol) was added to the catalyst suspension prepared above, RuNPs@CNCs, (5mL). To this mixture was added cyclohexanol (0.1 mmol) as internal standard. 0.5 equivalents of CS_2 with respect to ruthenium was added to the mixture. Then, the mixture was mounted onto a PARR multiple reactor system under H_2 pressure, 4 bars, 1000rpm, for 24 h at room temperature (optimized conditions). Afterwards, reaction mixture was extracted with diethyl ether and then injected on the GC-MS for monitoring the conversion.

Control Experiments for arene hydrogenation

Two types of blank experiments were conducted for toluene hydrogenation, under exactly similar conditions of temperature, pressure, metal loading and no. of equivalent used. In the first experiment, instead of the catalyst, RuNPs@CNCs, CNCs alone were used in the reaction. No conversion to the hydrogenated product was observed. In the second experiment, $RuCl_3.3H_2O$ was used instead of the catalyst. No conversion to the hydrogenated product was observed.

XPS

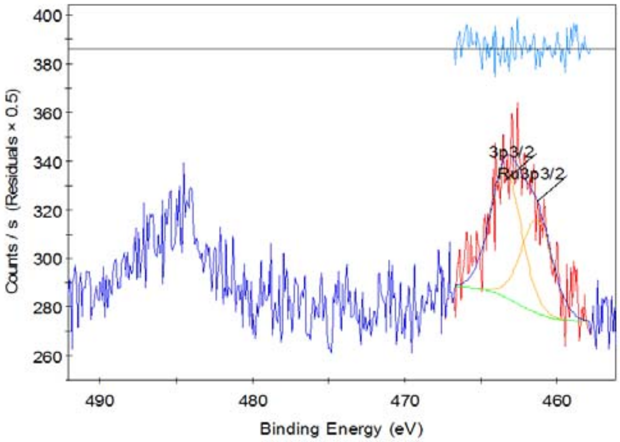

Figure S3: Ru 3p$_{3/2}$ peak at 461.27 eV confirms Ru (0).

TEM and EDS

5ul of samples were deposited on carbon film coated 400 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 allowed to dry under air before being 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.

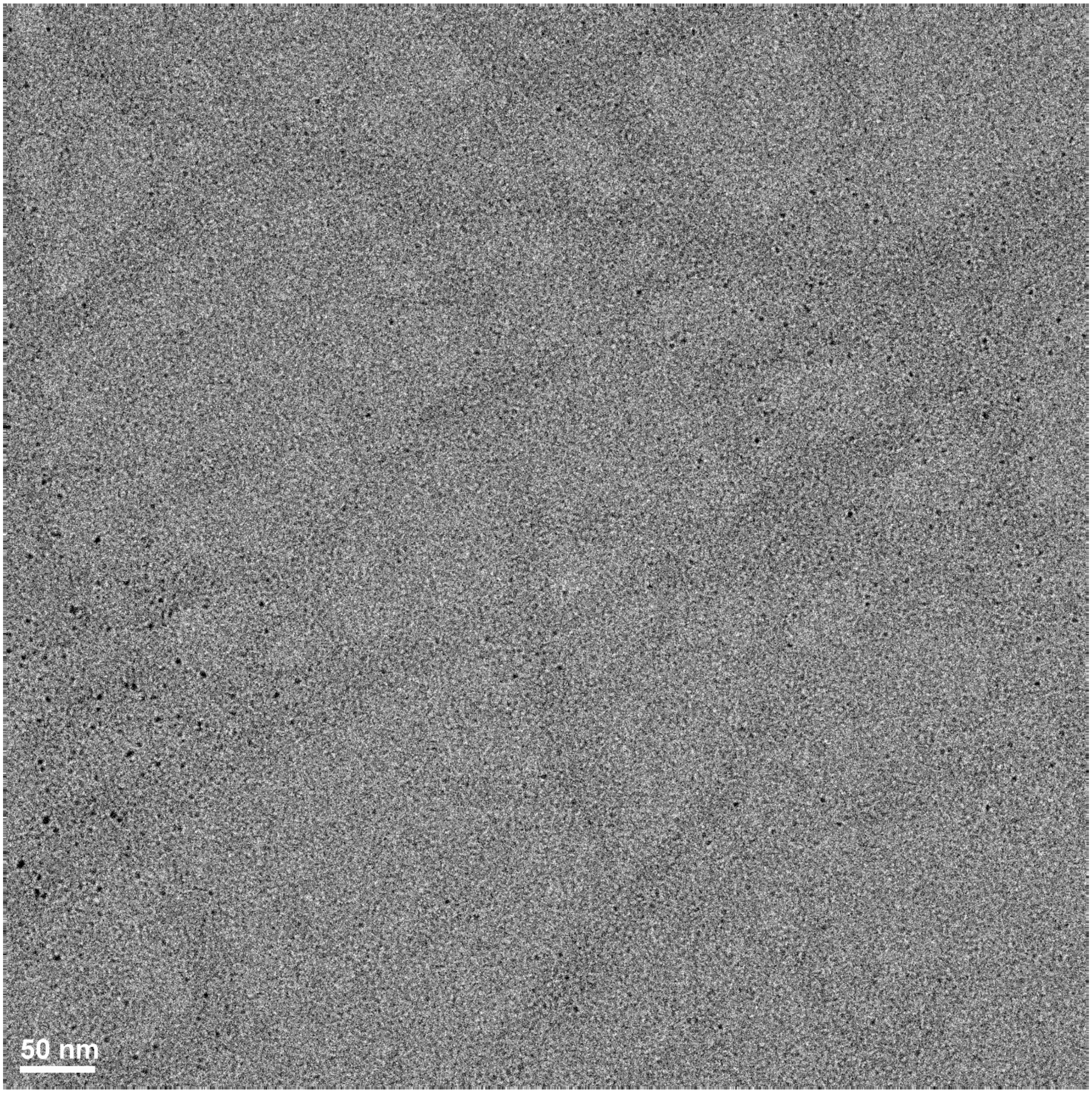

Figure S4: TEM of synthesized catalyst, RuNPs@CNCs

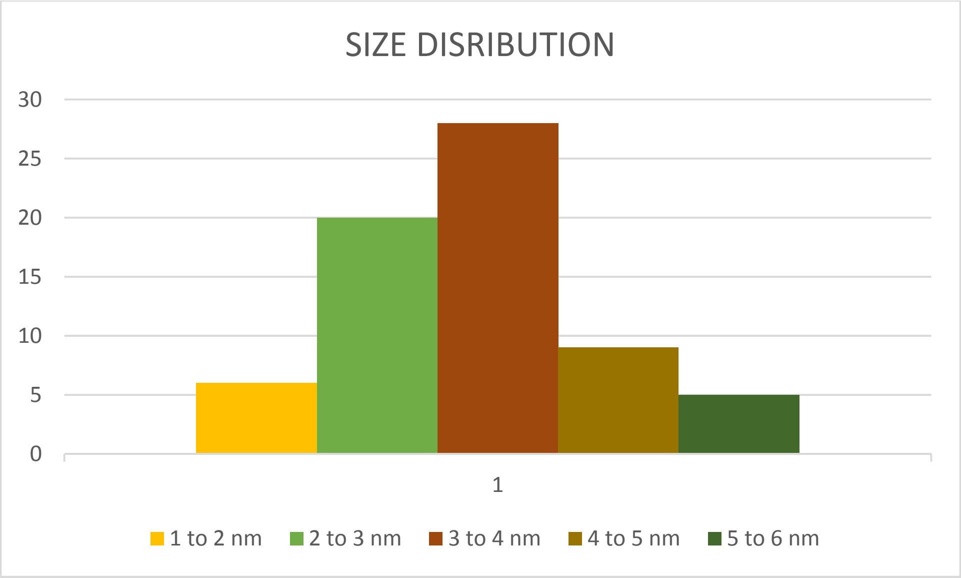

Figure S5: Size distribution of RuNPs@CNCs from TEM

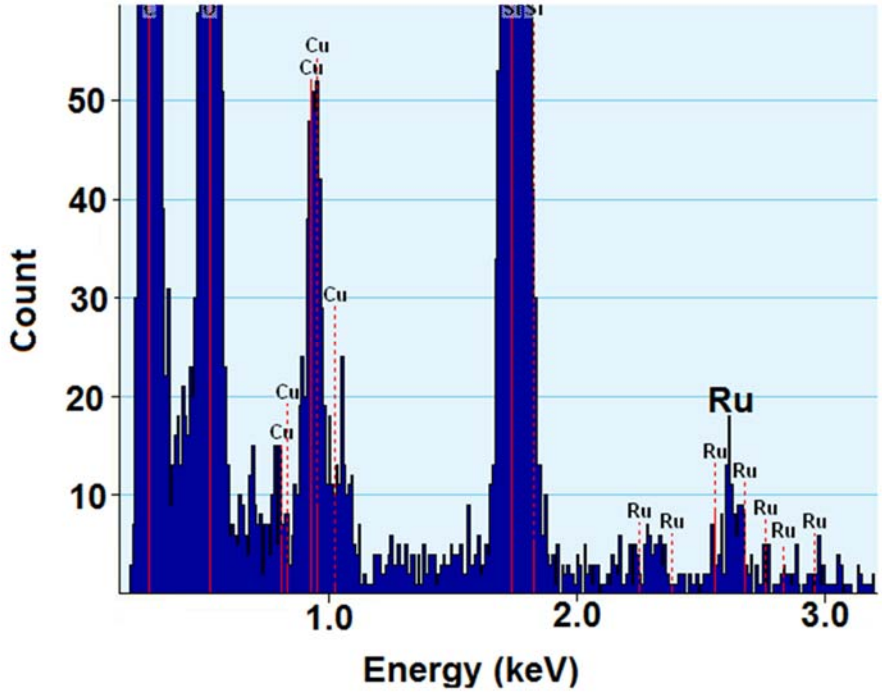

Figure S6: EDS confirming the presence of Ru

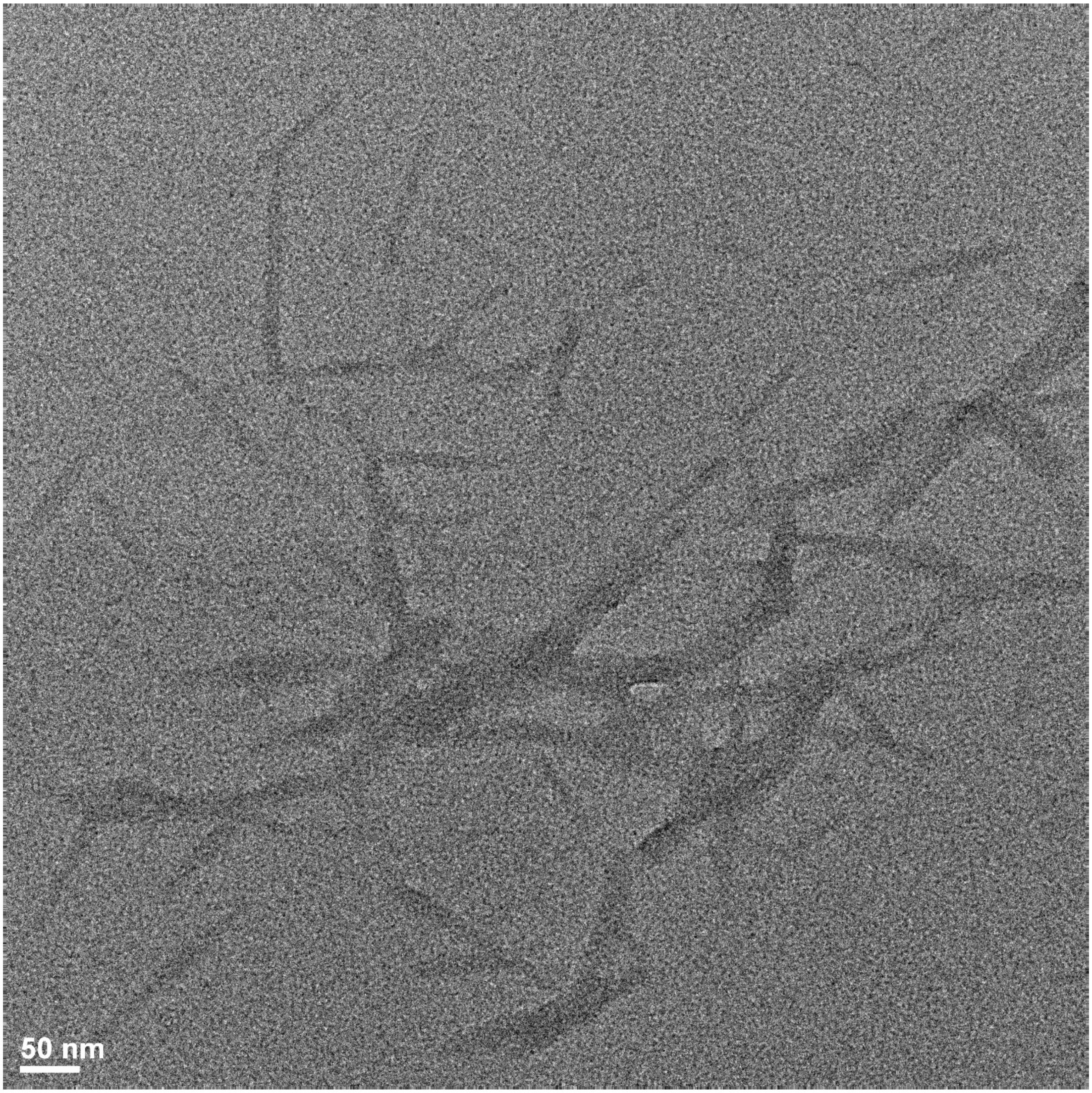

Figure S7: TEM of catalyst precursor, a mixture of $RuCl_3.3H_2O$ and CNCs. The image shows only well-dispersed CNCs, with presence of no Ru NPs.

Digestion of RuNPs@CNCs and the product for inductively coupled plasma – mass spectroscopy (ICP-MS) Measurements

The RuNPs@CNCs and product were digested in a 6:1 HCl/HNO_3 acid mixture (Fisher trace metal grade) in semiclosed HDPE vessels at 90 °C for 3 h following a similar procedure outlined by Hudson *et al*.[1] Samples were diluted to 1% HCl using Milli-Q water and analyzed by ICP-MS.

References

1. R. Hudson, V. Chazelle, M. Bateman, R. Roy, C. Li and A. Moores, *ACS Sustainable Chem. Eng.*, 2015, 3, 814-820.