

Supporting Information

1. Experimental

1.1. Materials

NaAuCl₄ * 2H₂O, was from Aldrich (99.99% purity). Commercial CNFs PR24-PS was supplied from Applied Science. PR24-PS consists of tubular fibers with an average diameter of 50± 20 nm and a specific surface area of 43 m²/g [J.P. Tessonnier, D. Rosenthal, T. W. Hansen, C. Hess, M. E. Schuster, R. Blume, F. Girgsdies, N. Pfaender, O. Timpe, D.S. Su, R. Schloegl, Carbon, 47, (2009), 1779.21] NaBH₄ of purity >96% from Fluka, polyvinylalcohol (PVA) 87–89% hydrolysed (M.W. 13,000–23,000) from Aldrich were used. NaOH from Fluka was of the highest available purity. Gaseous oxygen from SIAD was 99.99% pure.

1.2. Catalyst preparation

1.2.1 Carbon nanofibers functionalization

The functionalization of the CNFs was performed modifying the procedure report in [L. Prati, A. Villa, C. E. Chan-Thaw, R. Arrigo, D. Wang, D. S. Su Faraday Discuss. 2011, 152, 353-365.; R. Arrigo, S. Wrabetz, M. E. Schuster, D. Wang, A. Villa, D. Rosenthal, F. Girgsdies, G. Weinberg, L. Prati, R. Schlögl, D. S. Su, Phys. Chem. Chem. Phys. 2012, 14, 10523-10532;]. Carbon nanofiber were treated with HNO₃ according to the following procedure: a solution of CNFs in HNO₃ concentrate (10 g of CNF per liter of HNO₃) was kept at 353 K for 2 h under continuous stirring, then rinsed with distilled water, and finally dried at 373 K for several hours. N-containing CNFs were obtained from the pre-oxidized CNFs by thermal treatment (50 g for each batch) with NH₃ at 873 K for 6 h.

1.2.2. Au catalyst preparation

1.2.2.1 Au_{SI}

Solid NaAuCl₄ * 2H₂O (0.051 mmol) and PVA(1%wt) solution (Au/PVA 1/1 wt%) were added to 100 mL of H₂O. After 5 min, NaBH₄ (0.1 M) solution (Au/NaBH₄ 1/4 mol/mol) was added to the yellow solution under vigorous magnetic stirring. The ruby red Au(0) sol was immediately formed. Within a few minutes of sol generation, the colloid (acidified at pH 2, by sulphuric acid) was immobilised by adding the support under vigorous stirring. The amount of support was calculated as having a total final metal loading of 1 wt.%. After 2 h the slurry was filtered, the catalyst washed thoroughly with distilled water (neutral mother liquors) to remove PVA, and products deriving from the synthesis (Na, Cl) and dried at 80 °C for 4 h. The catalysts were labeled as Au_{SI}/N-CNF.

1.2.2.1 Au incipient wetness

Solid NaAuCl₄ * 2H₂O was dissolved in water (Au 10mg/mL). Enough of the metal-containing solution was added to the support to completely fill their pores, based on the total pore volume from nitrogen sorption analysis (5 mL/g). The amount of support was calculated so the final gold loading of 1 wt.% was obtained. The catalyst is then dried at 80°C for 2 h and reduced using NaBH₄ (0.1 M) solution (Au/NaBH₄ 1/4 mol/mol). The catalysts were labeled as Au_{IW}/N-CNF.

1.3. Oxidation procedure

Glycerol oxidation: reactions were carried out in a 30 mL glass reactor equipped with a thermostat and an electronically controlled magnetic stirrer connected to a 5000 mL reservoir charged with oxygen (3 atm.). The oxygen uptake was followed by a mass-flow controller connected to a PC through an A/D board, plotting a flow time diagram.

Glycerol 0.3 M, and the catalyst (substrate/ total metal = 1000 mol/mol) were mixed in distilled water (total volume 10 mL) and 4 equivalent of NaOH. The reactor was pressurized at 3 atm of oxygen and set to 50 °C. Once this temperature was reached, the gas supply was switched to oxygen and the monitoring of the reaction started. The reaction was initiated by stirring. Recycling tests were carried out under the same conditions (substrate/ total metal = 1000 mol/mol, 50 °C, 3 atm O₂, 1250 rpm, alcohol 0.3M, 2h). The catalyst was recycled in the subsequent run after filtration without any further treatment. Samples were removed periodically and analyzed by high-performance liquid chromatography (HPLC) using a column (Alltech OA-10308, 300 mm_7.8 mm) with UV and refractive index (RI) detection to analyze the mixture of the samples. Aqueous H₃PO₄ solution (0.1 wt%) was used as the eluent. Products were identified by comparison with the original samples.

1.4. Characterization

- a) The metal content was checked by ICP analysis of the filtrate or alternatively directly on catalyst after burning off the carbon, on a Jobin Yvon JY24.
- b) Morphology and microstructures of the catalysts were characterized by transmission electron microscopy (TEM) and high angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM). The powder samples of the catalysts were directly dispersed on copper grids covered with holey carbon film. A FEI Titan 80-300 image aberration corrected electron microscope, operating at 300 kV was used for TEM and STEM imaging. Electron tomography was performed by acquiring series HAADF STEM images with single axis tilting the sample from -76 to +76 degree at a tilting step of 2 degree. 3D structure of the supported catalysts was obtained after reconstruction from the series tilt images by using SIRT algorithm.
- c) X-ray photoelectron spectroscopy (XPS) data were collected using a PHI 3056 spectrometer with an Al anode source operated at 15kV and an applied power of 350 W. Samples were manually pressed between two pieces of indium foil; the piece of

In foil with the sample on it was then mounted to the sample holder with a piece of carbon tape (Nisshin E.M. Co. LTD). Adventitious carbon was used to calibrate the binding energy shifts of the sample ($C1s = 284.8 \text{ eV}$). [Moulder, J.F.; Stickle, W.F.; Solbol, P.E.; Bomben, K.D. Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer Corp. 1992.] High resolution data was collected at a pass energy of 5.85 eV with 0.05 eV step sizes and a minimum of 200 scans to improve the signal to noise ratio; lower resolution survey scans were collected at a pass energy of 93.5 eV with 0.5 eV step sizes and a minimum of 25 scans.

d) Surface area, pore size and pore volume were determined by low temperature N_2 adsorption using a SA3100 Coulter apparatus. Before measurement, samples were outgassed at 80°C for 3 h.

Table S1 Summary of binding energies, and moiety fraction, determined by XPS

Sample	C1s					Atomic % (C:N:O)
	C-C, C-H	C-O	C-N, C=O	C=C pi-pi	C ⁺ , C=N	
N-CNF (eV)	284.8	286.3	288.9	291.2	293.6	94.1: 4.5: 1.4
(%)	65.1	19.9	5.3	7.53	2.1	
	N1s			O1s		
	Pyridinic	Pyrrolic	NO	C=O	C-O	
N-CNF (eV)	398.6	400.5	404.2	531.2	533.5	
(%)	51.3	40.7	8.0	41.4	58.6	
	Au4f					Au [at%]
AuSI/N-CNF	84.1					2.8
(%)	100					
AuIW/N-CNF	<i>n.d</i>					0.1

Table S2. Statistical median and standard deviation of particle size analysis for Au based catalysts.

Catalyst	Statistical median (nm)	Standard deviation σ
Au _{SI} /N-CNF	3.2	0.9
Au _{IW} /N-CNF	3.4	1.0

Table S3 Stability test using Au_{SI}/N-CNF^a

<i>Au_{SI}/N-CNFs</i>	<i>Activity^b</i>	<i>Conversion after 1h</i>	<i>Selectivity (%)^c</i>			
			GLYA	TA	GLYCA	FA
Run 1	864	92	69	12	11	6
Run 2	853	93	68	12	9	4
Run 3	848	95	66	10	10	3
Run 4	862	94	69	11	11	2
Run 5	854	93	70	10	13	3
Run 6	843	92	71	12	14	2
Run 7	856	90	70	10	13	2
Run 8	852	91	72	11	14	4

a Glycerol 0.3M in water; 4eq of NaOH; metal/alcohol = 1/1000 mol/mol; 3 atm O₂; T=50°C;

b Mol of glycerol converted per hour per mol of metal, calculated after 15 min reaction

c Selectivity at 90% of conversion

GLYA=glyceric acid; TA=tartronic acid; GLYCA=glycolic acid; FA= formic acid

Table S4 Stability test using Au_{IW}/N-CNF^a

<i>Au_{IW}/N-CNFs</i>	<i>Activity^b</i>	<i>Conversion after 2h</i>	<i>Selectivity (%)^c</i>			
			GLYA	TA	GLYCA	FA
Run 1	1521	95	57	26	5	3
Run 2	1489	96	60	29	8	2
Run 3	1470	93	61	28	6	1
Run 4	1478	94	61	27	5	3
Run 5	1482	96	60	28	7	2
Run 6	1463	93	59	29	6	2
Run 7	1471	95	61	27	5	1
Run 8	1474	93	60	28	4	2

a Glycerol 0.3M in water; 4eq of NaOH; metal/alcohol = 1/1000 mol/mol; 3 atm O₂; T=50°C;

b Mol of glycerol converted per hour per mol of metal, calculated after 15 min reaction

c Selectivity at 90% of conversion

GLYA=glyceric acid; TA=tartronic acid; GLYCA=glycolic acid; FA= formic acid

Table S5 Liquid phase oxidation of 1,3 propanediol and ethylene glycol using Au_{PVA}/N-CNF and Au_{imp}/N-CNF

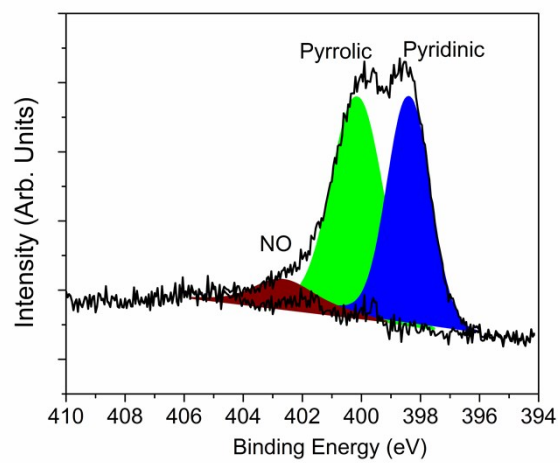
<i>Catalyst^a</i>	Substrate	Activity ^b	Conversion (%) After 2h	Selectivity (%)		
				3-hydroxy propionate	Malonate	Formate
Au _{IW} /N-CNFs	1,3 Propanedio l	1320	90	80	18	1
Au _{SI} /N-CNFs		651	88	94	3	2
Au _{IW} /N-CNFs	Ethylene glycol	952	86	83	15	2
Au _{SI} /N-CNFs		532	82	97	2	1

a Polyol 0.3M in water; 4eq of NaOH; metal/alcohol = 1/1000 mol/mol; 3 atm O₂; T=50°C;

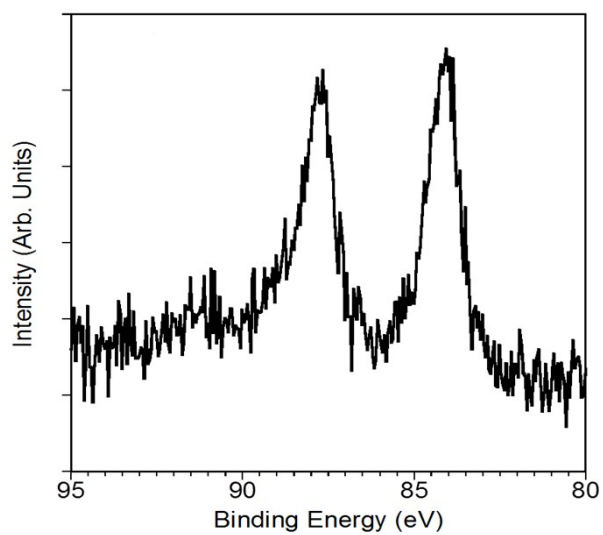
b Mol of polyol converted per hour per mol of metal, calculated after 15 min reaction

c Selectivity at 90% of conversion

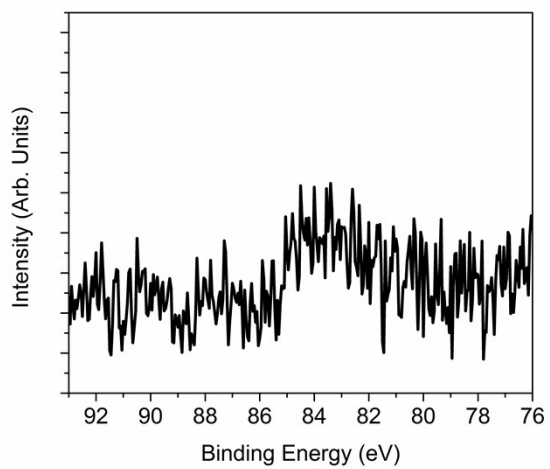
Figure S1 XPS data a) N1s of N-CNF, Au 4f of b) AuSI/N-CNF and c) AuIW/N-CNF



a)

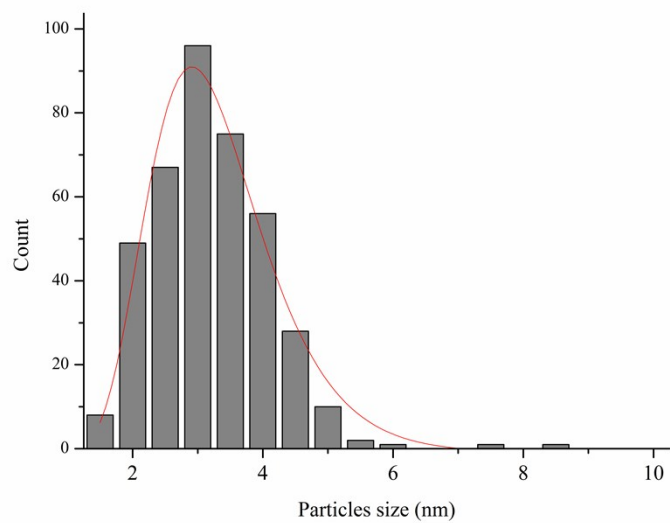


b)

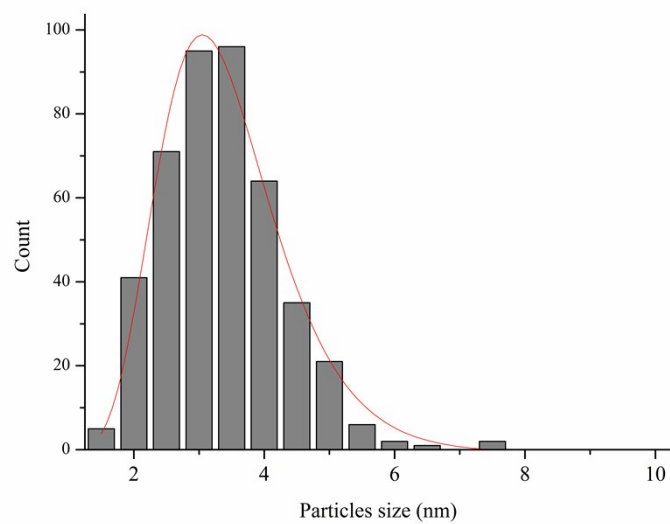


c)

Figure S2 Particle size distribution for a) Au_{SI}/N-CNF and b) Au_{IW}/N-CNF



a)



b)

Figure S3 Additional cross sectional slices derived from electron tomography showing Au particles prepared by impregnation situated on both inner- and outer-surfaces of CNF.

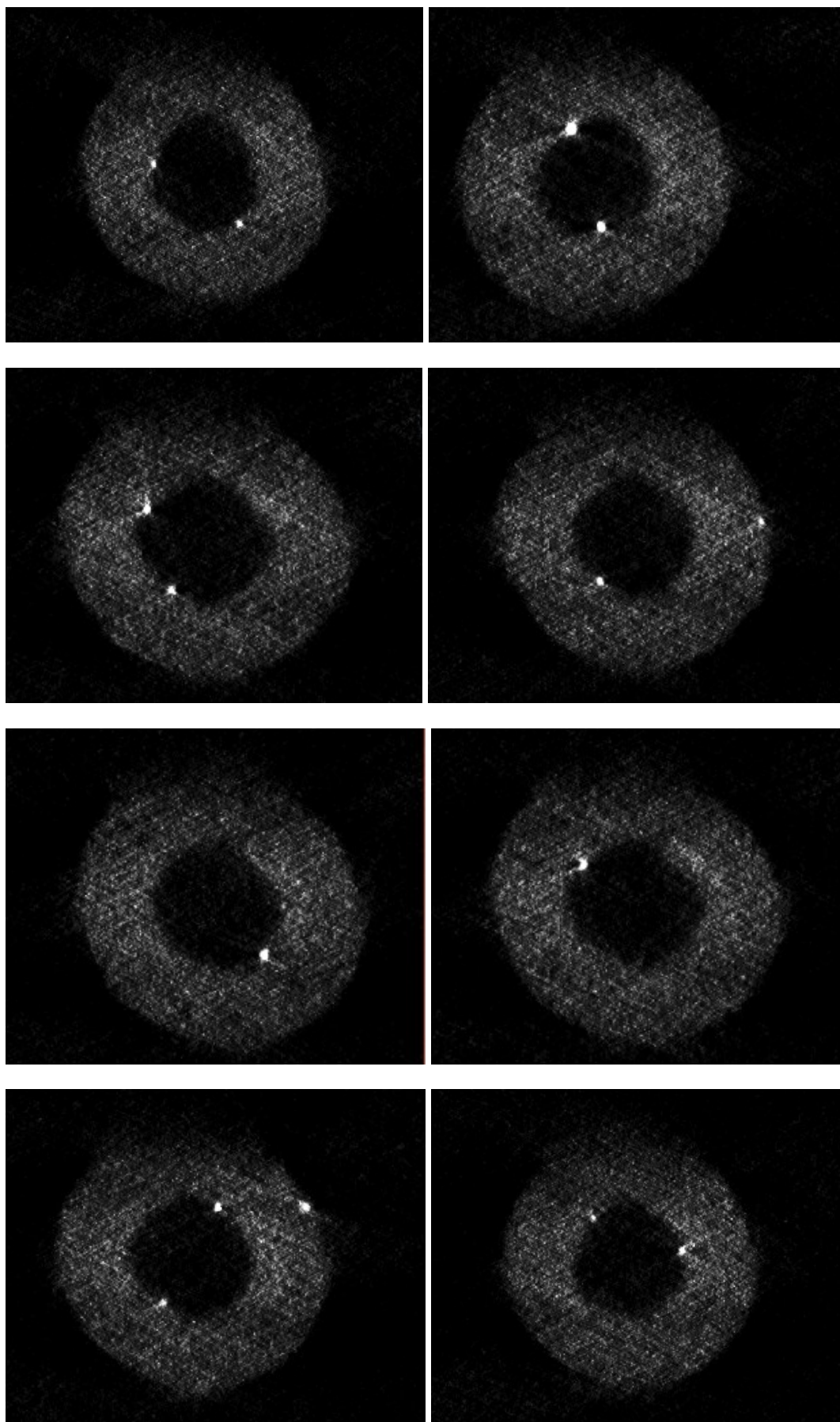


Figure S4 Additional cross sectional slices derived from electron tomography showing preformed AuSI particles exclusively situated on the outer surface of CNF.

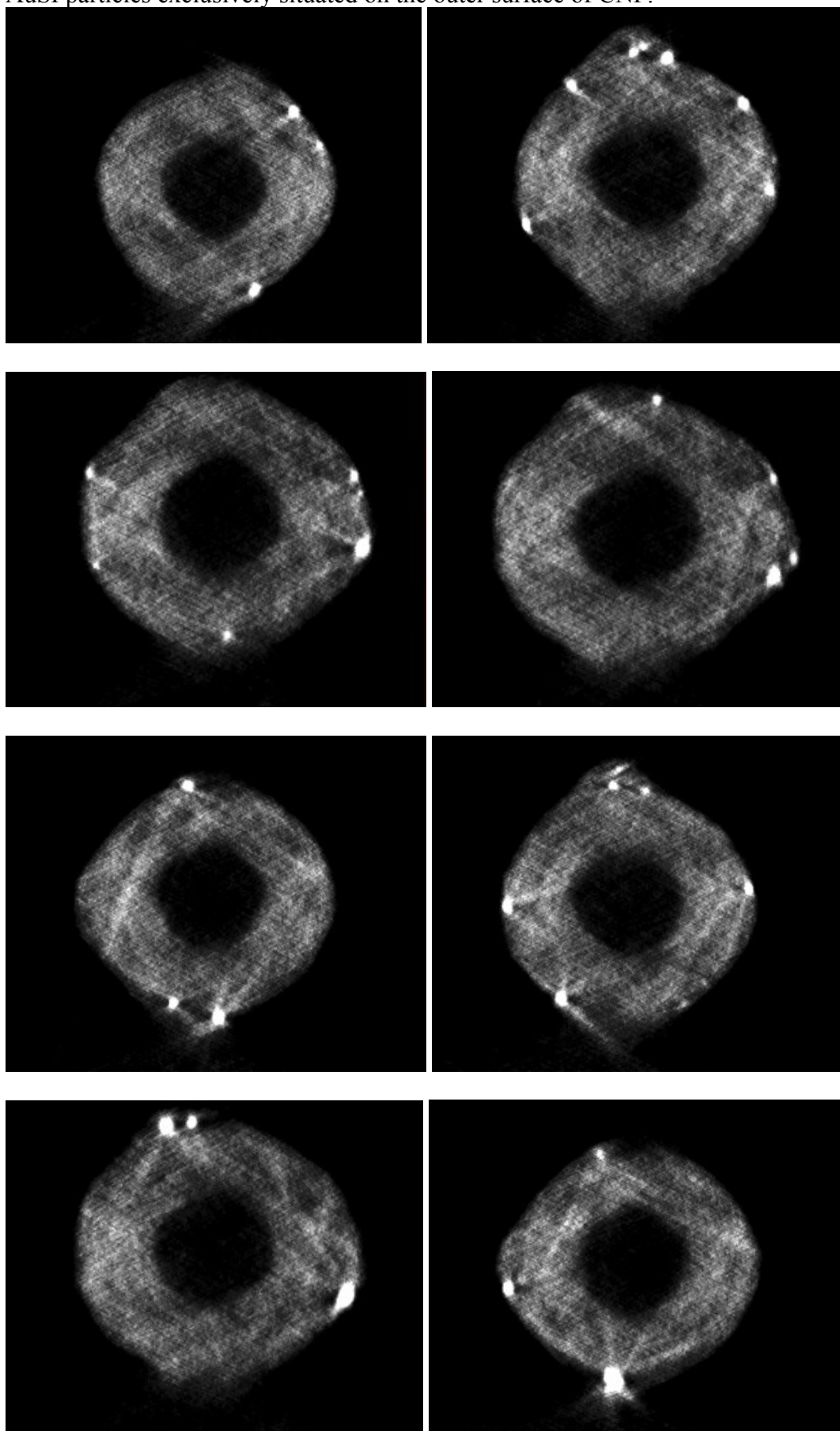
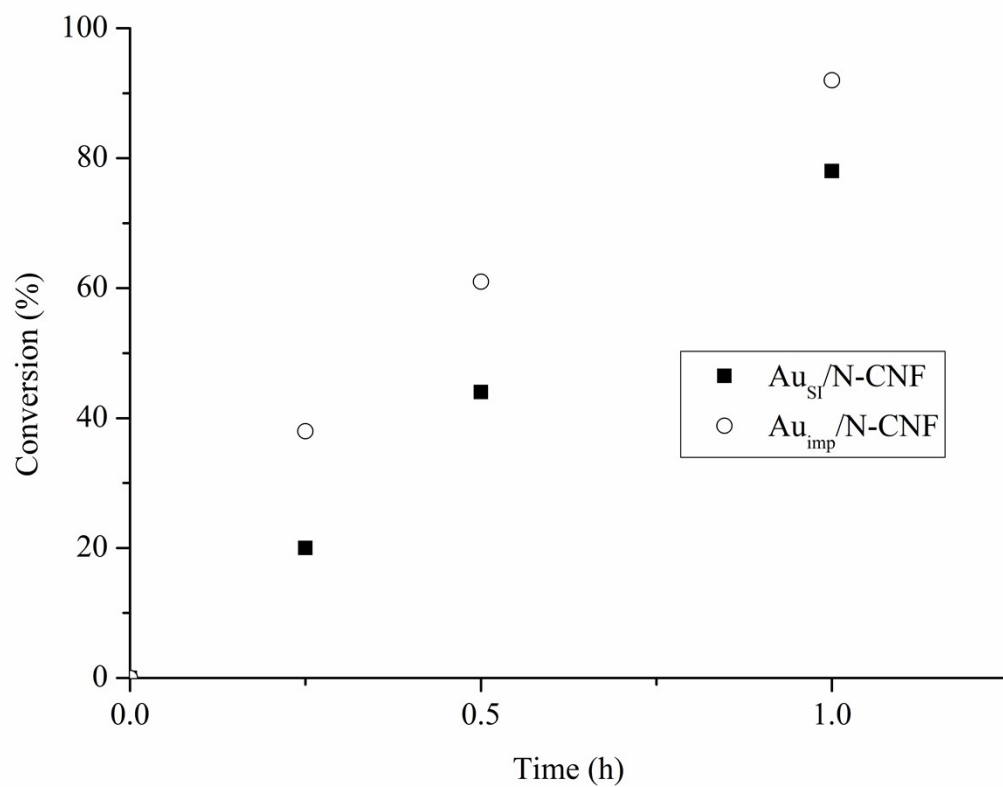


Figure S5 Reaction profile and selectivity at different conversion using $\text{Au}_{\text{SI}}/\text{N-CNF}$ and $\text{Au}_{\text{IW}}/\text{N-CNF}$



Scheme S1 Reaction scheme for glycerol oxidation

