Continuous Synthesis of Ruthenium Nanoparticles with Tuneable Sizes using Ruthenium Nitrosyl Nitrate precursor

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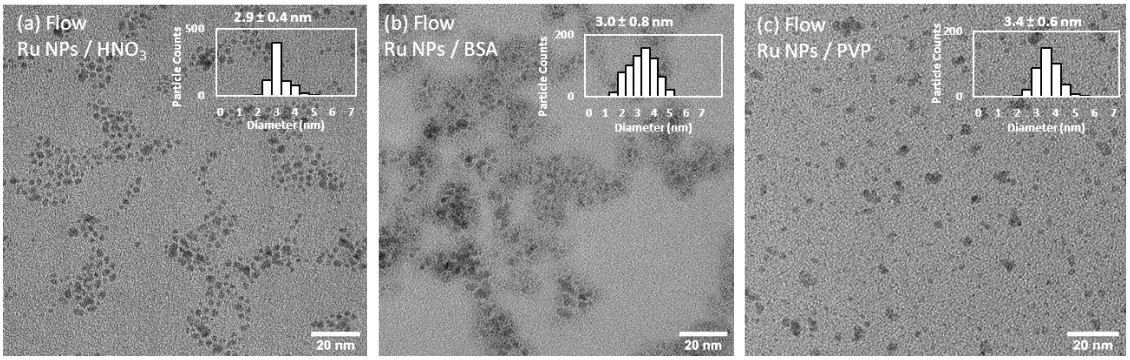
Supplementary information

Table S.1 TEM and DLS results of Ru NPs synthesised in flow and batch synthesis and collected in HNO_3, BSA and PVP post-synthesis.

Synthesis type	Acid/Stabiliser	Final pH with stabiliser	TEM results		DLS results		ZP Results	
			Average size (nm)	Standard deviation (nm)	Average size by number (nm)	Standard deviation (nm)	Average Zeta Potential (mV)	Standard deviation (mV)
Batch	HNO_3	1.2	4.0	0.7	7	1	+37	1
Flow	HNO_3	1.2	2.9	0.4	15	2	+32	2
	PVP	10.8	3.4	0.6	9	3	-35	2
	BSA	10.6	3.0	0.8	13	5	-39	4

Figure S.1: TEM images comparing batch and flow synthesis of Ru NPs collected in HNO_3, BSA and PVP post-synthesis. (a) TEM image of nanoparticles synthesised in batch collected in HNO_3 (C_f 0.1M). (b) TEM image of nanoparticles synthesised in flow and collected in HNO_3 (C_f 0.1M) (c) in BSA (Cf = 1 mg mL-1) and (d) in PVP (Cf = 2mg mL-1) (e) Lattice fringes from flow-synthesised Ru NPs in HNO_3 showing spacing of 0.22 nm corresponding to hexagonal close-packed Ru(0).



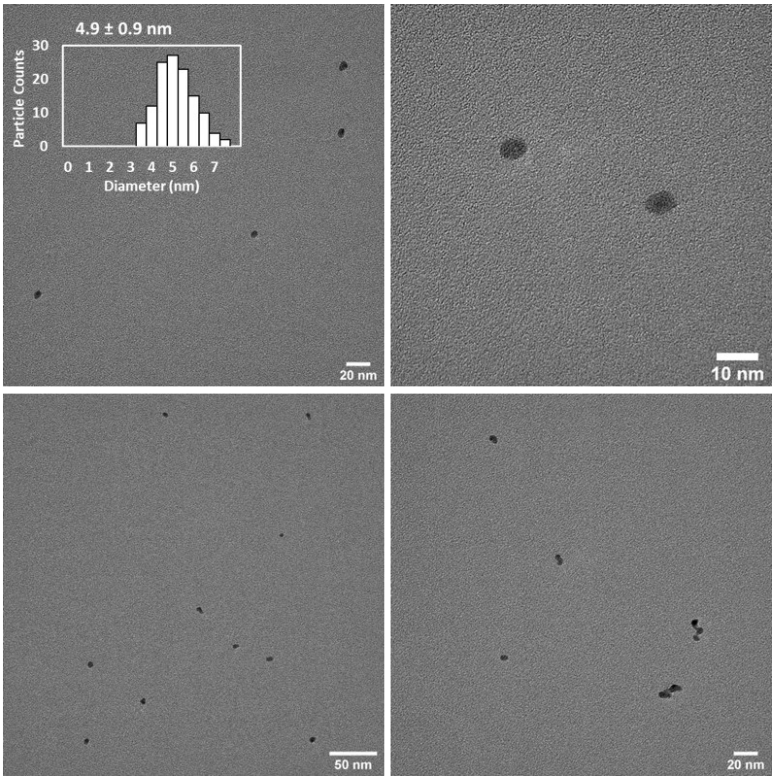


Figure S.2: Pd NPs synthesised in batch by mixing 2.5 mM of $K_2[Pd(NO)(NO_2)_4(NO_3)]$ (prepared from potassium tetranitropalladate as per *Griffith, Lewis and Wilkinson 1961*[59]) and 3 mM $NaBH_4$ at 25°C.

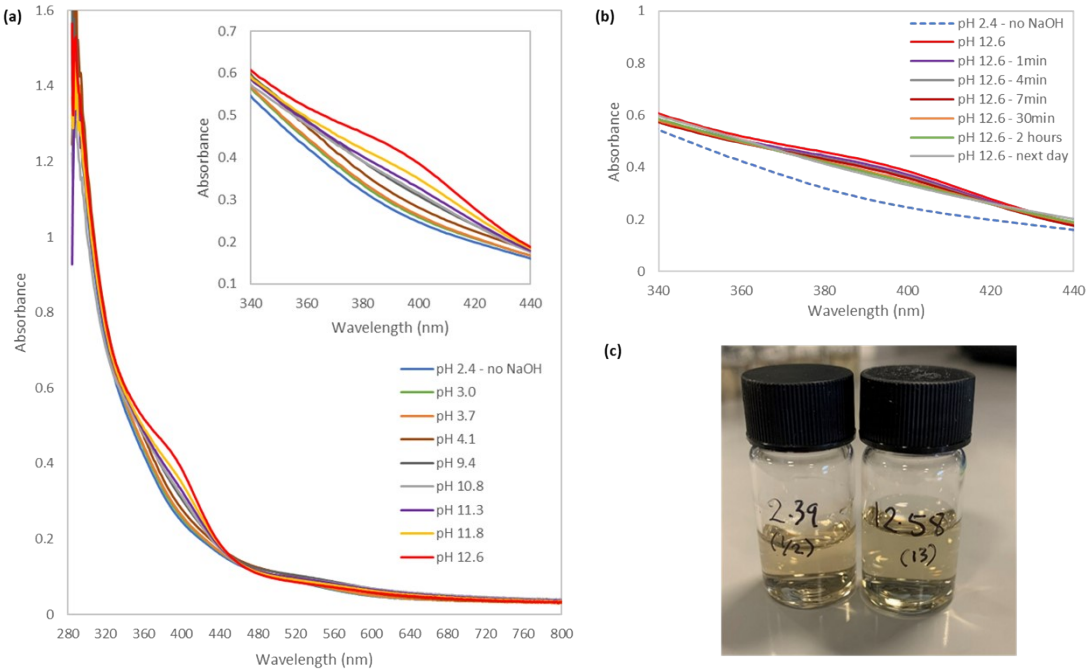


Figure S.3: Effect of pH on Ru precursor (a) UV-vis absorbance spectra for mixed solutions of 1.25 mM Ru(NO)(NO3)3 and NaOH at various final pH values, measured 10 seconds after mixing, from pH 2.4 (equivolume water addition in the absence of NaOH) to pH 12.6 (equivolume addition of 0.1 M NaOH) (b) relaxation of UV-vis shoulder for Ru solution with final pH 12.6 with time (c) Photo showing colours of Ru

solutions of final pH 2.4 and 12.6, taken 30 mins after conducting experiments. DLS measurements show no particles present.

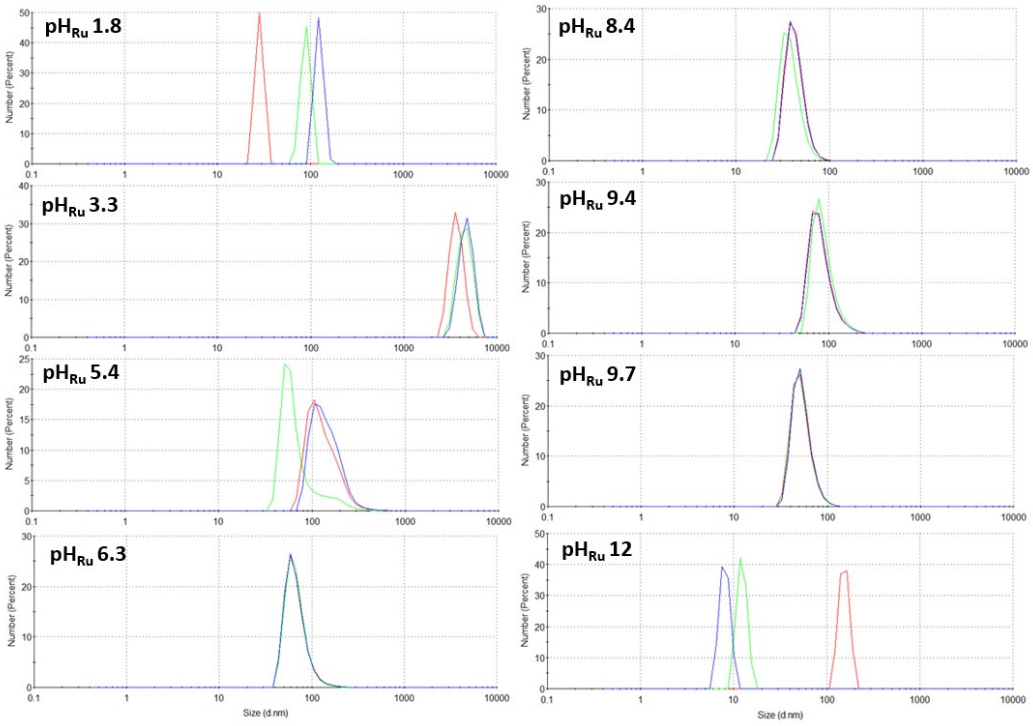
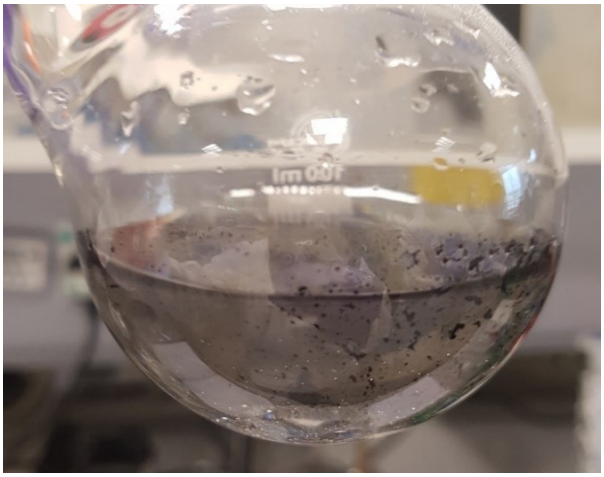


Figure S.4: Effect of pH on $Ru(NO)(NO_3)_3$ reducibility. DLS number size distribution plots for mixed solutions of 2.5 mM $Ru(NO)(NO)_3$ of varied starting pH values (pH_{Ru}) and 6.25 mM $NaBH_4$, measurements were conducted after 30 mins of mixing at 25°C. Repeatable results are observed only for solutions with pH_{Ru}



between 6.3-9.7.

Figure S.5: Evident precipitation during the reduction of $RuCl_3$ (2 mM, 40 mL) to form Ru NPs by dropwise addition of *powder-derived* $NaBH_4$ solution (0.1 M, 1.5 mL) at 0.2 ml/min.

Table S.2: Batch experiments with $RuCl_3$ (2 mM, 40 mL) with 8.5 mL of HCl of different concentrations, to which 1.5 mL of $NaBH_4$ was added either in one shot or dropwise, producing large DLS sizes and significant agglomeration after 24 h.

Concentration before mixing (mM)			$NaBH_4$ addition	Final concentration (mM)			Molar Ratio		Final pH	DLS average size by number (nm)
$RuCl_3$	$NaBH_4$	HCl		$RuCl_3$	$NaBH_4$	HCl	$NaBH_4$:Ru	HCl:$NaBH_4$		
2.00	100	35	One shot	1.6	3	5.95	1.88	2.0	1.90	152
2.00	800	140	One shot	1.6	24	23.8	15.0	1.0	2.42	345
2.00	100	35	0.3 ml/min	1.6	3	5.95	1.88	2.0	1.87	184
2.00	800	140	0.3 ml/min	1.6	24	23.8	15.0	1.0	1.92	252

Table S.3: TEM, DLS and Zeta Potential results of HNO3 stabilised Ru NPs from various size control experiments, Table 3.

Experiment	TEM results			DLS results			ZP results	
	Average size (nm)	Standard deviation (nm)	Number of particles counted	Average size by number (nm)	Standard deviation (nm)	Mean Count Rate (kcps)	Average Zeta Potential (mV)	Standard deviation (mV)
1	2.9	0.4	805					
2	3.9	0.5	531					
3	4.0	1.4	243					
4	2.1	0.3	320					
5	3.2	0.4	324					
6	3.0	0.5	563					

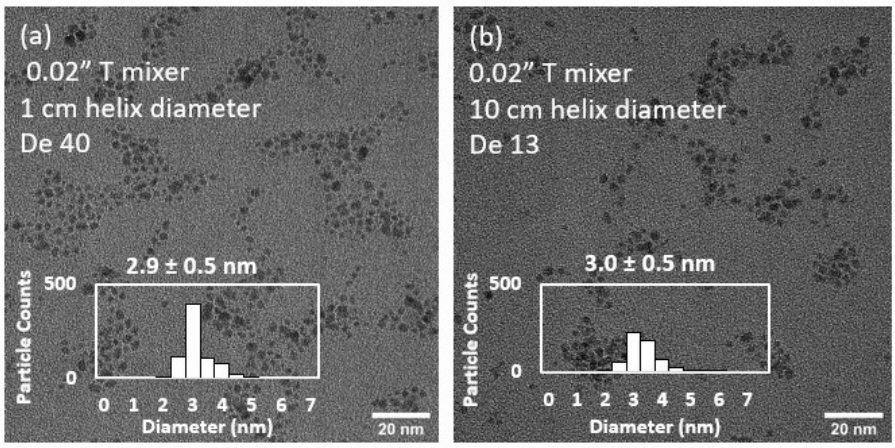


Figure S.6 Effect of reactor helix diameter on the size and distribution of continuously synthesised Ru NPs. Representative TEM images. Experiments 1 and 6, Table 3.