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Continuous synthesis of ruthenium nanoparticles with tuneable sizes using ruthenium nitrosyl nitrate precursor†

Joseph El-Kadi,  Eugenio Fenoaltea Pieche, Seung Woo Ko and Laura Torrente-Murciano  *

This paper presents a novel approach for the synthesis of ruthenium nanoparticles *via* the reduction of ruthenium nitrosyl nitrate with sodium borohydride in flow 3D helical reactors in the absence of capping ligands. Manipulating the pH-speciation of the ruthenium precursor and the fluid dynamics of the flow system allows for the synthesis of small nanoparticles and the tuning of average size with narrow size distributions ($2-4 \pm 0.5$ nm). A mechanism is proposed for the NP synthesis involving the formation of a stable ruthenium nitrite complex from the ruthenium nitrosyl nitrate precursor in the presence of sodium hydroxide, which avoids unwanted metal oxide hydrolysis or precipitation. In contrast, more conventional metal precursors such as chlorides or nitrates easily hydrolyse under basic conditions forming metal oxides or precipitates. We also demonstrate the need of achieving fast mixing of reactants (<50 ms) to enable a homogeneous nucleation under such fast reduction kinetics. This work is a demonstration of the need of combining reaction chemistry and engineering approaches on the synthesis of nanomaterials.

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Introduction

Ruthenium (Ru) is a transition and platinum group metal with a range of applications mainly in the electronics and catalysis sectors.¹ It is commonly used as an alloying agent to strengthen titanium, platinum and palladium to prepare wear-resistant electrical contacts.² In heterogeneous catalysis, ruthenium is gaining substantial attention for the synthesis³ and decomposition^{4–6} of ammonia, due to its interaction with nitrogen and ammonia being optimum according to the Sabatier principle. Indeed, ruthenium nanoparticles were at the centre of the so-called *second generation* of ammonia synthesis catalysts, however, they have only been deployed in isolated commercial cases due to its high cost and hydrogen poisoning at low conversion levels.⁷ In homogeneous catalysis, ruthenium and its complexes display activity for various reactions including acetic acid synthesis, water splitting, hydrogenation of C=C and C=O bonds, formic acid synthesis, alcohol dehydration, and oxidation reactions.⁸ Currently, the scarcity and high price of ruthenium, a rare metal, limits its widespread commercial application. Manipulating and maximising the nanoscale properties of

ruthenium has the potential to increase its industrial relevance, particularly for the catalysis of structurally sensitive reactions, where activity strongly depends on metal nanoparticle size within a certain range, usually below 10 nm.⁹

Traditional synthesis of heterogeneous catalysts relies on wetness preparation methods due to their simplicity and low cost¹⁰ where nanoparticles are synthesised directly on the surface of the support. The resulting size of the nanoparticles depends on a range of factors interacting in a complex manner, such as choice of metal precursor, pore volume and surface area of the support, support hydrophobicity and solvent, drying and calcination method. An alternative method is the synthesis of colloidal ruthenium nanoparticles and their post-synthesis deposition. A number of studies have demonstrated the synthesis of Ru NPs in a batch fashion, generally conducted *via* i. chemical reduction of a ruthenium salt with a borohydride agent^{11–15} or with a polyol (glycols or diols),^{14,16–21} and ii. organometallic decomposition of an organometallic ruthenium complex.^{22–33} However, past studies rely on the use of stabilisers and/or capping ligands to avoid agglomeration and control the size of Ru NPs,²⁰ with potential detrimental effects on their final catalytic activity due to the blockage of active sites.^{28,34} For example, Simakova *et al.*³⁴ reported the blocking of catalytic Ru active sites for the hydrogenation of arbinose and galactose

Department of Chemical Engineering and Biotechnology, University of Cambridge, Philippa Fawcett Drive, CB3 0AS, Cambridge, UK. E-mail: lt416@cam.ac.uk

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Allyami *et al.*³⁸ demonstrated an interesting example of Ru NP flow synthesis with the average Ru NP size changing from 2.9 ± 0.5 nm with Ru(acac) precursor *versus* 4.8 ± 0.5 nm with a different RuCl₃ precursor, however, oleylamine was used as a stabiliser in an organic solvent (toluene) under harsh conditions of 30 bar and 160 °C. The only example of ligand-free synthesis of Ru NPs was reported by Hu *et al.*³⁹ whereby 1.5 nm sized NPs were prepared *via* the polyol method with ethylene glycol and the addition of sodium hydroxide (NaOH). In this case, it is likely that NaOH electrostatically stabilised the Ru NPs during the synthesis, as suggested by other ligand-assisted Ru NP synthesis studies^{13,21} which have used acids or bases to induce an environment of electrostatic repulsion between colloidal NPs. Hu *et al.*³⁹ did not vary the average size of Ru, likely due to the limitations of batch synthesis to vary size while maintaining a narrow size distribution in the absence of capping ligands.

In this work, we present a new method to prepare colloidal ruthenium nanoparticles with precise sizes using a continuous/flow synthesis strategy in the absence of capping ligands. The Ru NPs are synthesised in a 3D microscale coiled flow inverter reactor (CFIR) *via* the reduction of ruthenium nitrosyl nitrate with sodium borohydride, producing smaller average sizes than in batch. The pH speciation of the metal precursor is found to be just as important as the kinetics of nucleation and growth. A mechanism is proposed for the NP synthesis involving the formation of a stable ruthenium nitrite complex in the presence of sodium hydroxide, which avoids unwanted metal oxide hydrolysis or precipitation. Manipulating the fluid dynamics of the flow system allows for the tuning of average size with narrow size distributions from 2.1 ± 0.1 nm to 2.9 ± 0.5 nm to 3.9 ± 0.5 nm. This demonstrates a departure from traditional Ru NP synthesis methods and presents a strategy to isolate the parameter of nanoparticle size for size-effect catalytic investigations.

Materials

Ruthenium nitrosyl nitrate solution ($\text{Ru}(\text{NO})(\text{NO}_3)_3$, 1.5 w/v% in dilute nitric acid), *alkaline* sodium borohydride solution (NaBH_4 , ~12 wt% in 14 M sodium hydroxide), *powdered* sodium borohydride (NaBH_4 , $\geq 98.0\%$), sodium hydroxide solution (NaOH , 0.1 M, 95–100%), *powdered* sodium hydroxide (NaOH , 97%), polyvinylpyrrolidone powder (PVP, average M_r 40 000), and bovine serum albumin powder (BSA, lyophilized, $\geq 96\%$) were purchased from Sigma Aldrich. Nitric acid solution (HNO_3 , 1 M) was purchased from Fisher Scientific. All chemicals were used without further purifications within 3 months of purchase to ensure fresh solutions free of degradation. Ultra-high-purified 18.2 M Ω cm MilliQ water was used in preparing all solutions and washing.

Synthesis of colloidal Ru NPs

Ruthenium nanoparticles (Ru NPs) were synthesised *via* wet reduction of ruthenium precursors ($\text{Ru}(\text{NO})(\text{NO}_3)_3$ and RuCl_3) using NaBH_4 as a reducing agent. In a typical flow synthesis, 2.5 mM $\text{Ru}(\text{NO})(\text{NO}_3)_3$ and 6.25 mM of *alkaline* NaBH_4 aqueous solutions were each fed at 115 mL h^{-1} by a Chemyx Fusion 6000 syringe pump through a continuous coiled flow inverter reactor (CFIR) (Fig. 1).

The precursors entered a 0.02-inch T-mixer in a *crossflow* configuration, where the Ru-containing stream entered the system perpendicular to the resulting direction of flow. The resulting solution passed through the CFIR, consisting of 3.16 m of perfluoro alkoxy (PFA) tubing (0.02-inch inner diameter and 1 cm outer diameter) coiled around a 3D printed support (printed using a Formlabs Form 2 3D stereolithographic printer with a high temperature resin and 0.1 mm resolution). Both the mixer and the reactor were immersed in a water bath maintained at 25 °C. Steady-state conditions were assumed after 2 min of operation, after which samples were collected. For post-synthesis

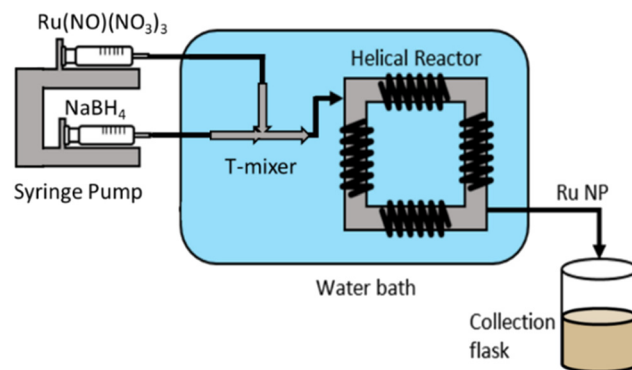


Fig. 1 Ru NP continuous reactor set up: two syringe pumps control flowrates of $\text{Ru}(\text{NO})(\text{NO}_3)_3$ and NaBH_4 solutions. Reactants were mixed with a T-mixer in crossflow configuration and the resulting solution passes through the coiled flow inverter reactor (CFIR).

changes the rotation axis of the Dean vortices, breaking the stagnant zones as well as promoting a more homogeneous residence time distribution across the cross-sectional area under laminar flow.³⁵

A total flowrate of 230 mL min⁻¹ (equal flowrate for both inlet streams) results on a Reynolds number of 179 and a Dean number of 40, confirming laminar flow and the formation of Dean vortices respectively. An initial reaction concentration of Ru(NO)(NO₃)₃ and NaBH₄ of 1.25 mM and 3.13 mM were used respectively, the latter containing 0.03 M NaOH. As a result, the pH during the synthesis is 9.5, avoiding the fast deposition of NaBH₄ by hydrolysis under non-alkaline conditions (eqn (2)).⁴³

$$\text{NaBH}_4 + 4\text{H}_2\text{O} \rightarrow \text{H}_3\text{BO}_3 + \text{NaOH} + 4\text{H}_2 \quad (2)$$

Under these conditions, a residence time of 10 s led to the formation of Ru NPs with small sizes and narrow size distribution (2.9 ± 0.4 nm, Fig. 2a) which were electronically stabilised in the presence of HNO_3 in the receiving outlet vial (0.1 M final concentration).^{13,21,39} The acidic conditions also quenched the reaction by rapidly decomposing any NaBH_4 remaining in the solution. To confirm such rapid quenching provided by HNO_3 , no reaction or change in color was observed when the precursors were mixed directly into a nitric acid solution, with no solid particles detected under DLS. The Ru NPs collected in HNO_3 presented a zeta potential value greater than +30 mV (Table S1†), suggesting high colloidal stability.^{44,45} In addition, such electrostatic stabilisation facilitated their imaging as the particles were less obscured than ligand-stabilised NPs counterparts (Fig. S1†). Representative TEM images are shown in Fig. 2a where the lattice spacings of 0.21 nm (Fig. 2b) confirmed the presence of hcp Ru(0) metal.^{46–48} Electrostatic stabilisation is expected to be less detrimental in the final application than chemically bound ligands (*e.g.* catalytic applications). Full conversion of the Ru precursor after 10 s of residence time was confirmed by precipitating the particles by their destabilisation at a pH of 6–8 (using NaOH). After centrifugation, the colourless supernatant solution was analysed by ICP-MS showing very low Ru content (0.08, 0.3 and 0.6 ppb) indicating 98–99% conversion of the initial Ru precursor. Analyses were done in triplicates.

For comparison purposes, a batch synthesis of Ru NPs was carried out under the same conditions by quickly mixing the Ru- and the NaBH₄-containing streams together in a round bottom flask reactor. Similarly, the reaction was quenched after 10 s by adding a HNO₃ solution (0.1 M final concentration). A representative picture of the resulting Ru NPs is shown in Fig. 2c, showing slightly larger sizes and a broader size distribution (4.0 ± 0.7 nm) than the flow-synthesised counterpart. As demonstrated below, these differences are associated to the enhanced mixing rate achieved in flow reactors in comparison to batch ones.

As mentioned above, the pH during the flow synthesis was 9.5. This value was a result of mixing the $\text{Ru}(\text{NO})(\text{NO}_3)_3$

Characterisation

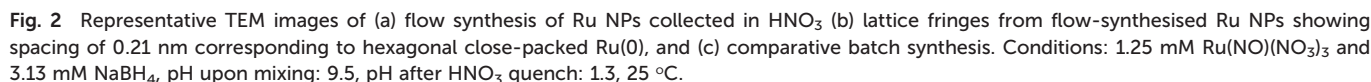
pH measurements were carried out with a Fisherbrand™ accumet™ XL150 pH Benchtop Meter with a Tris-compatible double junction refillable glass-body pH electrode. Synthesised Ru NP suspensions were analysed by Dynamic Light Scattering (DLS) to estimate average size and zeta potential (ZP) to assess colloidal stability using a Malvern Zetasizer Nano S90 instrument equipped with a 633 nm laser. Ultraviolet-visible (UV-vis) spectrometry was conducted with an Agilent Cary-60 UV-vis spectrometer. Transmission Electron Microscopy (TEM) was conducted with a Talos, FEI microscope (200 kV), with samples prepared by drop-casting 3 µl of colloidal Ru NP suspension onto a carbon-coated copper TEM grid (400 mesh, Agar Scientific) and drying naturally for 30 min. Particle size distribution histograms were constructed using ImageJ open-source software using a minimum of 200 nanoparticles from at least 3 TEM images taken from different mesh sections of the TEM grid. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) was used to measure the concentration of Ru in solution using a Thermo-Fisher Nexion 2000-S machine.

Results and discussion

Ruthenium nanoparticles were synthesised in a flow reactor by reduction of $\text{Ru}(\text{NO})(\text{NO}_3)_3$ with NaBH_4 to produce $\text{Ru}(0)$ as shown by eqn (1).⁴⁰

$$8\text{Ru}^{3+} + 3\text{BH}_4^- + 12\text{H}_2\text{O} \rightarrow 8\text{Ru} + 3\text{B}(\text{OH})_4^- + 24\text{H}^+ \quad (1)$$

The two reactants were introduced perpendicular to each other through a T-mixer (Fig. 1) and then passed through a coiled flow inverter reactor (CFIR). This reactor geometry promotes internal rotation of the fluid by the curvature of the channel through the creation of Dean vortices.^{41,42} In addition, the periodic 90° change in the direction of the flow



To investigate the effect of the reducibility of Ru(NO)(NO₃)₃ speciation at different pH values, the pH of 2.5 mM Ru(NO)(NO₃)₃ precursor solution was first varied between 1.8 to 12 and subsequently 6.25 mM NaBH₄ solution (aqueous solutions of powdered NaBH₄ in the absence of NaOH) was added (note that these conditions are similar to those in the flow synthesis above). Observations are summarised in Table 1. The most alkaline Ru(NO)(NO₃)₃ solution (pH 12) experienced no colour change within 20 min of NaBH₄ addition with DLS results showing poor repeatability, substantially low count rates, and unstable raw correlogram plots due to low Ru conversion. However, agglomerates were observed after 20 h, suggesting that under alkaline conditions, the reduction reaction is very slow. Similar observations took place on the other side of the pH spectrum. The most acidic Ru(NO)(NO₃)₃ solution (pH 1.8) experienced no subsequent colour change after 20 min of NaBH₄ addition and showed unstable DLS results, also indicating low Ru conversion. No agglomerates or colour change were observed even the following day, likely because the very acidic conditions instantly hydrolytically decomposed the NaBH₄ solution, preventing any further reduction, as well as the high stability of Ru(NO)(NO₃)₃ under these conditions as previously discussed.

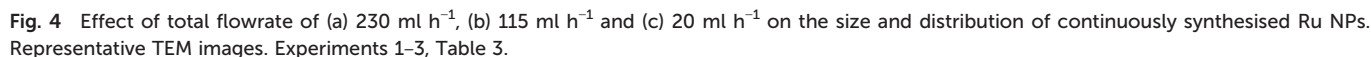
Before mixing				Initially after mixing				
Ru(NO)(NO ₃) ₃ solution		NaBH ₄ solution		[Ru] mM	[NaBH ₄] mM	pH of solution 10 s after NaBH ₄ addition	Molar ratio of NaBH ₄ : Ru	Visible agglomeration after 30 min (Y/N)
[Ru] mM	pH	[NaBH ₄] mM	pH					
2.5	1.8	3.8	12.3	1.25	1.9	2.4	1.5	N
		4.4	12.2		2.2	3.5	1.8	N
		5.0	12.4		2.5	5.3	2	N
		5.6	12.5		2.8	8.4	2.3	N
		6.3	12.5		3.1	9.5	2.5	N
		6.9	12.6		3.2	10.3	2.8	Y
		7.5	12.6		3.8	11.0	3	N

The relatively fast reduction of $\text{Ru}(\text{NO})(\text{NO}_3)_3$ by NaBH_4 at a pH of 9.5 and the differences in Ru particle size in batch and flow reactors indicate that mixing time (*i.e.* the time required to achieve homogeneous mixing between both reactant streams) has a similar scale to the reaction time, an aspect usually overlooked in material synthesis.⁵⁵ In these cases, a fast-mixing rate is critical to trigger a homogeneous nucleation of Ru NP in the whole reactor volume leading to narrow size distributions.⁵⁶ Flow reactors are particularly suited to evaluate transport phenomena effects as their fluid dynamics are well-defined and can be manipulated easily by simply varying their design and operating conditions. To understand these effects, Ru NPs were synthesised in flow systems under the same conditions (1.25 mM $\text{Ru}(\text{NO})(\text{NO}_3)_3$ and 3.13 mM NaBH_4 , pH upon mixing: 9.5, 25 °C), but with varying reactor design parameters and operating conditions as summarised in Table 3, alongside resulting Ru particle size and distribution (TEM). Further DLS and zeta potential characterisation is provided in Table S3.† The disparity between the DLS and TEM results in Table S3† are because the DLS measurements have a low limit of particles size of ~10 nm.⁵⁷ DLS measures the hydrodynamic sizes of particles, being particularly sensitive to the presence of large particles

Based on these initial screenings, a NaBH_4 :Ru molar ratio of 2.5 is selected for flow synthesis to achieve sufficient conversion of the Ru precursor while avoiding the formation of agglomerates or the stable Ru nitrite complex. Both NaBH_4 :Ru molar ratios of 2.3 and 2.5 are deemed suitable, however, 2.5 is selected based on ensuring that there is an excess of NaBH_4 to effectively reduce the stable Ru nitrite complex which forms in the presence of NaOH. This ratio of

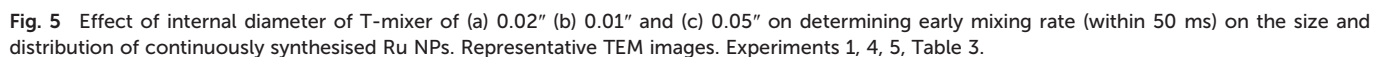
Experiment	Total flowrate (mL h ⁻¹)	Residence time (s)	Reactor details ^a				TEM results	
			T-mixer	Helix diameter (cm)	Reynolds number	Dean number	Average size (nm)	Standard deviation (nm)
1	230	10	0.02''	1	179	40	2.9	0.5
2	115	20	0.02''	1	90	20	3.9	0.5
3	20	115	0.02''	1	16	4	4.0	1.4
4	230	10	0.01''	1	179	40	2.1	0.3
5	230	10	0.05''	1	179	40	3.2	0.4
6	230	10	0.02''	10	179	13	3.0	0.5

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In each size control experiment, the Ru NPs were electronically stabilised in the presence of HNO_3 in the receiving outlet vial (0.1 M final concentration). The acidic conditions also quenched the reaction by rapidly decomposing any NaBH_4 remaining in the solution. Keeping constant the flow system configuration and decreasing the total precursors flowrate from 230 to 115 ml h^{-1} leads to an increase in particle size from 2.9 ± 0.4 to 3.9 ± 0.5 (experiments 1 and 2, Table 3, Fig. 4). Further decrease of the total flowrate to 20 ml h^{-1} does not lead to further increases of sizes but instead a considerably broader size distribution, 4.0 ± 1.4 nm (experiment 3, Table 3, Fig. 4). This relative upper limit of ~ 4 nm agrees with other observations in the literature using NaBH_4 as a strong reducing agent.^{11,13-15} Increasing total flowrate has two convoluted effects on mixing. On one hand, it increases the early mixing in the T-mixer promoted by a higher level of engulfment of the streams.⁵⁹ On the other hand, it also promotes a higher level of mixing in the reactor itself by increasing the magnitude of the Dean vortexes formed in the coiled flow inverter reactor. Dean vortexes consist of the

To decouple the mixing effects in the T-mixer and the reactor, the total flowrate (230 mL h⁻¹) and reactor configuration (CFIR) was fixed, while the internal diameter of the T-mixer was varied between 0.01 and 0.05" (experiments 1, 4 and 5, Table 3, Fig. 5). The Ru NPs sizes increased from 2.1 to 2.9 and 3.1 nm as the T-mixer internal diameter increased from 0.01 to 0.02 to 0.05" respectively. In all cases, a similar size distribution of ± 0.3 –0.4 nm was measured (Fig. 5). As the fluid dynamics in the reactor is the same in the three experiments, with constant Reynolds and Dean numbers (179 and 40 respectively), any differences in size can only be attributed to the early mixing in the T-mixer, within the first 50 ms. As a result, it can be concluded the faster the mixing rate (*i.e.* rate at which homogeneous mixing



is achieved), the faster the average nucleation rate which leads to a higher number of nuclei and consequently a smaller resulting size of Ru NPs. Similar conclusions have been confirmed using computational fluid dynamic simulations for gold nanoparticles³⁷ and perovskite nanocrystals.⁶⁰

On the other hand, keeping constant the flowrate (230 mL h⁻¹) and T-mixer (0.02") but varying the curvature of the coiled reactor from 1 cm to 10 cm (experiments 1 and 6, Table 3) led to almost negligible differences in the resulting particle size and distribution (2.9 ± 0.4 nm and 3.0 ± 0.5 nm respectively, Fig. S6†) despite the considerable differences in Dean number (40 and 13 respectively) and thus, radial mixing in the reactor. It is important to note that the flow inversions were omitted in the latter experiment to further minimise any radial mixing. The high early mixing rate promoted at high Reynolds number in the T-mixer likely leads to a homogeneous distribution of nuclei across the reaction volume promoting homogeneous growth in the reactor, independent on any further passive mixing during this stage (>50 ms). Further comparison of experiments 2 and 3 (Table 3) where the synthesis of Ru NPs were carried out in the same flow set-up but with decreasing flowrates (58 and 10 mL h⁻¹ leading to 3.9 ± 0.5 nm and 4.0 ± 1.4 nm respectively) demonstrates that in order to achieve a homogeneous growth in the reactor and thus, narrow size distribution, it is critical to have previously achieved a high level of mixing during the nucleation stage. It must be noted that due to the absence of stabilisers, there is also the possibility that the inner walls of the reactor function as sites for heterogeneous nucleation of the NPs. Further research is needed to investigate this synthetic avenue.

Conclusions

A novel flow synthesis method has been developed to produce electrostatically stable small and tuneable (2–4 nm) Ru nanoparticles with narrow size distributions in the absence of capping ligands. The use of Ru(NO)(NO₃)₃ as a ruthenium precursor avoids the formation of aggregates during the synthesis due to the formation of a stable intermediate ruthenium nitrite (NO²⁻) from the nitrosyl group (NO) in the presence of NaOH. An understanding of the speciation of this ruthenium precursor as a function of pH reveals that a balance in NaOH concentration is required. An NaOH deficit results in the fast degradation of the sodium borohydride reducing agent while an NaOH excess slows down the reduction. The synthesis of small and narrow size dispersed nanoparticles under such fast reduction kinetics requires a fast early mixing (<50 ms) to enable a fast and homogeneous nucleation across the reaction volume. Manipulating such early mixing (e.g. by varying the mixer configuration for the inlet streams) leads to size tuneability between 2 and 4 nm. Homogeneous growth is also required to achieved narrow size distributions, but this can happen either in the mixer or throughout the whole synthesis time.

Conflicts of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

Acknowledgements

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