

A simple setup miniaturization with multiple benefits for Green Chemistry in nanoparticle synthesis

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ABSTRACT

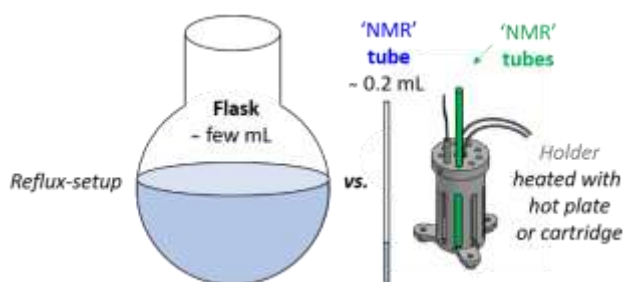
The development of nanomaterials often relies on wet-chemical syntheses performed in reflux-setups using round-bottom-flasks. An alternative approach to synthesize nanomaterials is presented that uses glass tubes designed for NMR analysis as reactors. It uses less solvent, less energy, generates less waste, provides safer conditions, is less prone to contamination and is compatible with high throughput screening.

Introduction. Nanomaterials (NMs) are used in multiple applications ranging from catalysis, optics, medicine to water/air treatments.¹⁻³ Due to strong structure-property relations on the nanoscale, the careful and rational synthesis of NMs is important. Consequently, the controlled syntheses of NMs has been increasingly addressed as a key component of Green Chemistry.⁴⁻⁸ The need for protocols generating less waste and increasing safety has been stressed.^{6,7} A focus is often given to the solvents and reactants to select,⁹ and the use of microwaves or ultrasound, considered more energy efficient.⁸ The development of setups such as flow (micro)reactors is also useful to minimize waste and simplify NM synthesis.¹⁰⁻¹² However, “despite these advantages, microfluidic systems have yet to be extensively adopted by the colloidal nanomaterial community”.¹³ The above strategies often require specific equipment and expertise, which may account for their relatively limited implementation. Simpler miniaturized systems with high throughput potential would gain to be proposed.

Wet-chemical methods often show promising scalability while being easily implemented in most modern laboratories¹⁴⁻¹⁶ NMs with various compositions, sizes and structures can be prepared by wet-chemical syntheses, which results in tuned NM properties to best match specific requirements

for various applications.¹⁶⁻¹⁸ The control over NM features is achieved by tuning experimental parameters, e.g. temperature, concentration of reactants, type of reactants or solvent composition. However, studying and understanding how synthetic parameters influence the NMs produced is often limited by the time and resources required to make a single batch of NMs. In a textbook approach using reflux-setups, 10-100 mL of solvent is typically required and only one experiment can be performed every few hours per setup, **Scheme 1**. To understand how NM structures change with synthetic parameters, alternative high throughput strategies are needed.

As an alternative to the conventional reflux-setup, we propose to use as reactors glass tubes designed for nuclear magnetic resonance (NMR) measurements^{19,20} **Scheme 1**. The multiple advantages of this simple alternative in Green Chemistry for NM synthesis^{6,8} are illustrated with the preparation of four different nanoparticles (NPs): gold (Au), iridium (Ir), osmium (Os) and copper sulfide (Cu_{2-x}S). Although precious metal (PM) based NPs are made of non-renewable resources, they remain key materials in multiple applications,⁷ e.g. to develop fossil-fuel-free technologies for energy conversion,¹⁷ and as models to understand NM formation.²¹ Even minor improvements in PM NP syntheses can have significant scientific, economic and ecologic impact.



Scheme 1. Moving from *round-bottom-flask* to *NMR tube* glassware for greener NM syntheses and studies.

Au NPs. Au NPs have been a case study for Green Chemistry in NM synthesis.⁷ In particular, the Turkevich synthesis is widely reported, where typically 0.1-0.5 mM HAuCl₄ is reduced in water close to the boiling point by trisodium tricitrate.^{22,23} The investigation of the many parameters controlling the properties of the Au NPs²² would be gained from high throughput approaches using less solvent than the typical 200-500 mL required. The Au NPs obtained performing the Turkevich synthesis in 500 mL (reflux-setup) or 0.2 mL (NMR tube) lead to the same NP size within the error of measurement by TEM, **Figure 1**. A range of alternative Au NP syntheses use organic solvents such as oleylamine and relatively high temperature.²⁴ Syntheses at higher temperature, e.g. 200 °C, are also possible since nut and ferrule can be used to close the NMR tube, **Figure 1C**.

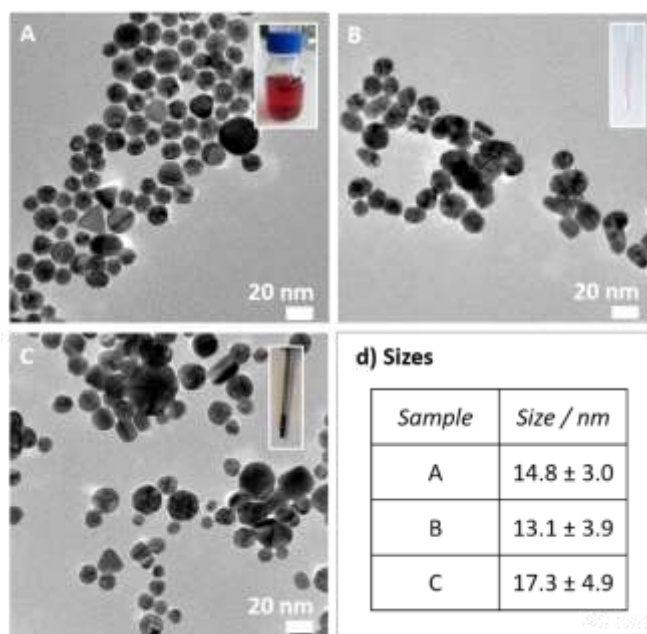


Figure 1. TEM micrographs of Au NPs obtained from 0.125 mM HAuCl₄ in water in presence of 2.2 mM trisodium citrate at 100 °C for 1 hour for a total volume of (A) 500 mL and (B) 0.2 mL. (C) TEM micrographs of Au NPs obtained using oleylamine at 200 °C as solvent in 0.3 mL. Insets

are pictures of the resulting colloidal dispersions. TEM acquired at different magnifications and the related size distribution are available in **Figure S4**. (D) Table of the related size distributions.

Ir NPs. We reported a surfactant-free colloidal synthesis of PM NPs directly relevant for the industry,^{17,25} performed at low temperature ($< 80\text{ }^{\circ}\text{C}$) in alkaline mono-alcohols like methanol or ethanol, leading to high catalytic activity for the oxygen evolution reaction,^{17,26} without intensive washing or purification steps, thus already addressing few Green Chemistry principles for NP synthesis.^{6,7,27} The Ir NPs are in the range 1-2 nm across a wide range of experimental parameters.²⁸ To possibly achieve size control, investigating high concentrations of precursor and long synthesis time are reasonable options. Using a microwave or even a classical reflux-setup, it is arguably challenging to investigate these hypotheses due to safety concerns, higher precursor cost and pressure on lab space and equipment access. Using NMR tubes, safe and simple time resolved studies over weeks of synthesis using high precursor concentrations (100 mM IrCl_3) are easily performed, **Figure S5**. It is found that NPs with an average size of 1.6 nm are obtained even at high concentration and long synthesis time, **Figure 2**.

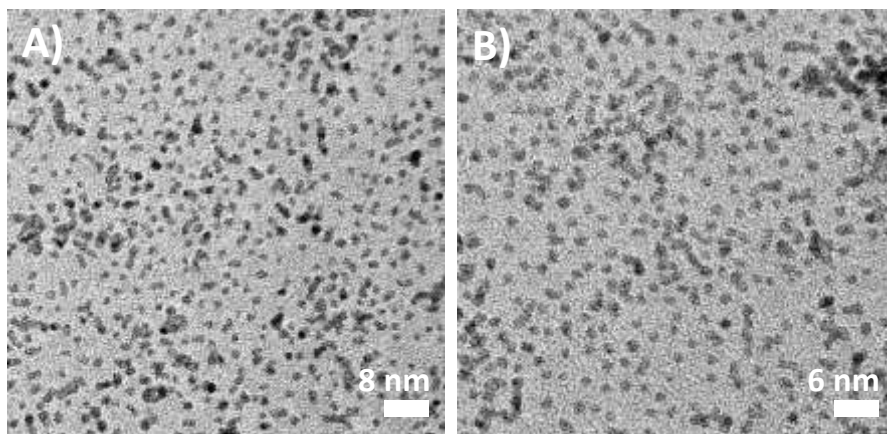


Figure 2. TEM micrographs at different magnification of Ir NPs obtained from 100 mM IrCl_3 in 1 M NaOH in methanol at $60\text{ }^{\circ}\text{C}$ for a week for a total volume of 0.2 mL. See also Figure S5-S6.

Os NPs. Os NP synthesis has received less attention than other PMs.²⁹⁻³¹ Taking advantage of the small volume of solvent needed, we investigated the surfactant-free synthesis of Os NPs using a high precursor concentration in simple low boiling points solvents such as a mixture of methanol and water. TEM micrograph of the resulting materials obtained for a one-week long synthesis starting with 100 mM of OsCl₃ show that small size NPs, ca. 1.6 ± 0.4 nm in diameter, are obtained **Figures S7-S8**. Although Os NPs are made of non-earth abundant element, the small size Os NPs obtained by a surfactant-free approach are relevant to develop more sustainable energy conversion systems to move away from fossil-fuels based energy.³²⁻³⁴

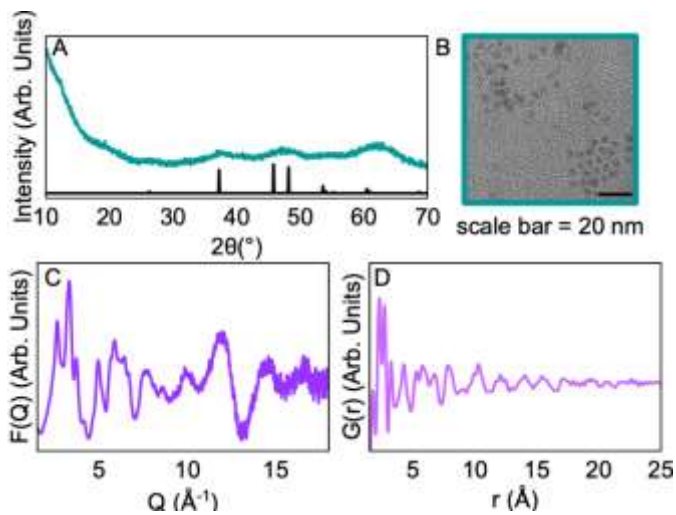


Figure 3. Characterisation of Cu_{2-x}S NPs obtained in an NMR tube setup. (A) Using a lab-source XRD instrument (blue) compared to a calculated diffraction pattern of β -chalcocite taking the space group P6₃/mmc (black). (B) TEM micrographs of the washed NPs. Scale bar is 20 nm. (C) Displays of the F(Q) and (D) PDF (G(r)) of X-ray total scattering data collected at Argonne national lab at beamline 11-ID-B.

Cu_{2-x}S NPs. Cu_{2-x}S NPs have applications in batteries,^{35,36} sensors³⁷ and as an oxygen evolution reaction catalyst.³⁸ The analysis with a lab-source XRD instrument of the NPs synthesized in the NMR tubes suggests that small Cu_{2-x}S NPs were formed, **Figure 3A**. TEM analysis shows a size of 4.5 ± 0.9 nm, **Figure 3B** and **Figure S9**. While some features are observed in the XRD pattern in **Figure 3A**, the broadening of Bragg peaks from these small NPs makes any structural investigation challenging. In contrast, the use of the NMR tube makes further characterization straightforward, e.g. using synchrotron scattering techniques, as many measurements can be done directly on the sample in the NMR tube. For instance, the as-prepared samples in closed NMR tubes can be sent to synchrotron for X-ray total scattering with pair distribution function (PDF) analysis. The PDF can be understood as a histogram of atom-atom distances in the material. In **Figure 3C,D** are reported the $F(Q)$ (data in reciprocal space) and $G(r)$ (data in real space) of the reaction solution after background subtraction. The PDF analysis confirms that the NPs can be described by a β -chalcocite model in space group $P6_3/mmc$ ³⁹ with deviations in the local structure, **Figure S10**.

Benefits. Using 3 mm diameter NMR tubes, allows to perform syntheses with volume as low as 0.1 mL, **Figure S3**. This low volume reduces the amount of waste generated and allows to investigate the effect of high concentration solutions towards scaling-up.^{7,16} Sample holders can be designed to perform several experiments at a time (up to 9 experiments per holder in the current design) allowing high throughput screening. Small volume also allows safer operating conditions. As a result, both long(er) and an increased number of experiments can be performed with minimal lab space and little equipment required, while optimizing the energy needed to heat up the solutions. Temperature control is achieved by either using the temperature control of a heating

plate or using dedicated heating cartridge with a temperature controller to control the heating rate, **Figures S1-S2**. Septa can be used to close the NMR tubes to control the atmosphere, alternatively, nut and ferrules can be used for higher pressure experiments, **Figure S1**. The length of the NMR tube provides an area of contact with cool air to function under reflux conditions. This area can also be cooled down, e.g. with a fan or dedicated water-cooling devices. It is worth stressing that the synthesis can be performed with stirring by simply using a commercially available stirrer bar (e.g. 8 mm x 1.5 mm) in the NMR tube, **Figure S3**.

Further considerations. As illustrated above, a range of characterization can be performed. Including advanced characterization at synchrotrons, see also discussion in SI.⁴⁰ NMR tubes make it possible to use a clean vessel for each experiment. This alleviates the need to clean glassware, thus limiting the chemical waste generation related to cleaning steps, e.g. using *aqua regia* for Au NPs.⁴¹ Importantly, it alleviates the question of cross contamination, thus addressing the well-known issue of reproducibility in NM science, often ascribed to chemical impurities from various sources.⁴² NM synthesis can be sensitive to variations of room temperature or room light, and the stability overtime of the chemicals and/or precursors solutions can be an issue.⁴³ These variables may be challenging to control across long periods of time when a study would last for instance several weeks or months. This drawback is alleviated with NMR tubes as reactors since several experiments including controls can be performed at the same time. Energy is saved because several experiments are heated all at once. The ease of simply performing relatively long experiments is also a positive feature towards improved yield of the precursor conversion to NMs.

It could be argued that due to the small diameter of the NMR tubes, capillary effects might come into play and the actual temperature-pressure during reaction might not be well-known. This issue of variability in physical parameters of reactors, e.g. heat transfer properties, stirring etc., is the

same for most scaling up to date, e.g. when moving from reflux-setups to larger scale reactors. In this respect, the use of NMR tubes reactors remains a convenient and *green* approach to screen the influence of experimental parameters.

A final practical consideration is storage and reuse. The small NMR tubes are easily stored due to their small diameter and length. The 18 cm long NMR tube are easily cut with a commercially available glasscutter to save more space. The open end of the glass can be sealed by melting with a torch (e.g. butane torch), for instance when toxic reagents and/or air sensitive compounds are involved. The samples can be safely and space-efficiently stored for further analysis. Additionally, the cut section of the NMR tube can be cleaned and sealed by melting one extremity to be re-used as a new miniaturized vessel.

Conclusions. A simple alternative to the classical round-bottom flask synthesis approach to prepare NMs is presented. By using commercially available NMR tubes, a miniaturized vessel suitable for the synthesis of various NMs is readily obtained. This approach complies with several of the principles of Green Chemistry for NM synthesis.^{6,7} This approach is therefore directly relevant for academic research and research and development but also educational purposes.

With the increasing interest in machine learning and artificial intelligence, large datasets are needed to feed algorithms.⁴⁴ The present approach allows for high throughput (pre)screening. Characterization remains a limiting factor - although enough material is obtained for characterization like TEM, XRD or PDF and naturally NMR characterization - but the variety of approaches and the expected improvements in this area of research are promising.^{6,19,45,46} It is expected that the simple alternative proposed here will also be relevant for various syntheses of molecules and other chemical reactions.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge. Materials and Methods, TEM and PDF characterization, Figure S1-S10, further discussion (PDF).

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Author Contributions

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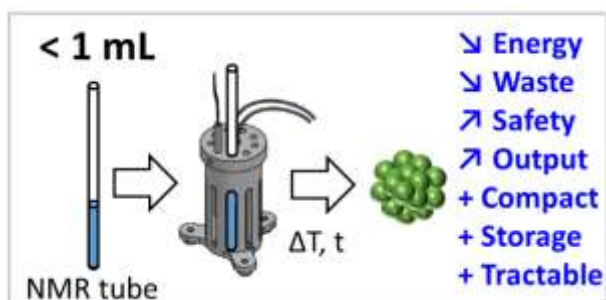
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TABLE OF CONTENT



SYNOPSIS

Small diameter NMR tubes are ideal reactors to implement the Green Chemistry principles in wet-chemical nanomaterial synthesis studies.