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Continuous Production of Tailored Silver Nanoparticles by Polyol Synthesis and Reaction Yield Measured by X-ray Absorption Spectroscopy: Towards a Growth Mechanism.

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ABSTRACT: In this paper two complementary topics are discussed: (i) the continuous production of silver nanoparticles (AgNPs) and (ii) the measurement of reaction yield by X-ray Absorption Near Edge Spectroscopy (XANES). The continuous *polyol synthesis* of AgNPs in grams amount and in the size range of 7-104 nm was carried out in the Segmented Flow Tubular Reactor (SFTR). Particle size was tailored by controlling the synthesis parameters such as temperature, reactant concentrations, and polyvinylpyrrolidone (PVP) molecular weight. The continuous production was tested for 4 h and the product has shown constant particle size distribution over the whole production time. Reliable continuous production of 2.3 g h^{-1} of about 100 nm AgNPs can be achieved with a lab-scale SFTR. The produced particles were fully characterized with respect to size, size distribution and chemical purity. To better understand the growth mechanism, synchrotron-radiation high-resolution X-ray diffraction and X-ray absorption spectroscopy data were collected directly on the AgNPs suspension. In particular, from XANES experiments the conversion yield of Ag^+ to Ag^0 was measured. The results are consistent with a two steps process where PVP controls the particle nucleation while growth is ensured by thermally induced ethylene glycol oxidation.

1. Introduction

Over the last couple of decades, noble metal nanoparticles have attracted significant interest in science and industry due to their wide range of applications. Thanks to their interesting optical properties, AgNPs have gained a lot of attention in applications such as surface-enhanced Raman spectroscopy,^{1,2} optical sensing,³⁻⁵ electronics⁶ and plasmonic enhancement of absorption.⁷ Noble metal nanoparticles have also excellent surface properties that find application in catalysis⁸. AgNPs in the size range 20-50 nm are required for the preparation of conductive paste for ink-jet⁹⁻¹² or screen printing^{13,14} as well as for joining of power electronics components.¹⁵⁻¹⁷ For these

latter applications, a narrow particle size distribution is mandatory because few larger particles cause nozzle clogging or defects in the conductive wires or joining layers. Excellent electrical and thermal properties, very close to the silver bulk values, are obtained upon sintering. When flexible organic substrates are used (e.g. polymeric films) the sintering temperature has to be as low as possible, ideally below 250 °C. Sintering temperature decreases with particle size driving the technology toward Ag NPs. Nevertheless, very high solid loads (>50 wt%) are required in metal pastes in order to produce optimal electrical and thermal conductivities but such ultrafine particles are very difficult to retrieve quantitatively from the synthesis mother solution. Thus, a trade-off between a low sintering temperature and facile particle retrieving is for instance the use of larger particles (30-100 nm).

Moreover, AgNPs are particularly interesting as conductive filler for the preparation of composite materials with high dielectric properties. Epoxy-based composites using Ag as filler with dielectric constants up to 300 have been reported so far.^{18,19} For this application, AgNPs with an average size up to 200 nm and narrow particle size distribution are of great interest.

Liquid phase chemical reduction is a simple and popular method to prepare metal nanoparticles from salts, since no hazardous by-products are generated. Among these methods, the polyol synthesis, intensively investigated by Xia and co-workers,^{20,21} stands out as a convenient and environmentally friendly way to generate silver nanostructures.

Different stabilizers have been used in the polyol synthesis, which include polyacrylamide,²² polyacrylic acid (PAA)²³ and polyvinylpyrrolidinone (PVP).²⁴ By tuning the synthesis parameters such as concentration,²⁴ precursor addition rate and method, temperature²⁵, average molecular weight of the stabilizer,^{26,27} reactant stoichiometry^{28, 29} or additives,³⁰⁻³³ size and shape of the nanocrystals can be controlled.

One of the limitations in producing high quality Ag NPs is the poor control of mixing conditions, stirring efficiency, temperature inhomogeneity, heating and cooling rates, in the batch type reactors used. This hampers the reproducibility and product quality and uniformity.^{24, 34,35} Despite the influence of the aforementioned parameters, good product quality may be obtained when working with low reactant concentrations; the product quality degradation, such as particle size distributions broadening, becomes very pronounced when attempting to scale up e.g. by increasing the reaction volume or increasing the precursor concentration. The preparation of AgNPs in batch conditions with different reaction volumes show the differing product properties and indicate that the reproducibility of the small scale reaction cannot be obtained by simply increasing the reaction volume (see Supporting Information). The heat transfer in a small volume is more efficient than in a large volume, and this affects the nucleation process. The batch reaction at smaller reaction volume yields smaller particles since there is a more rapid nucleation due to the faster heating of the reaction mixture. This also manifests itself on the better particle size distribution achieved in small scale reactions. Overall, the obtained yields of the reactions were around 70 %. The difficulty of the upscaling of the reaction can also be seen in ref. [24] where the best particle variation coefficient was obtained at a silver nitrate concentration of around 31 mM. A further increase in the concentration, despite keeping the precursor ratio constant, led to a deterioration of the particle size distribution. A possibility to overcome scaling up problems is by multiplying or “numbering up” the small batch syntheses but can become cumbersome and expensive. An alternative is to use a continuous flow reactor. Few attempts for the continuous production of Ag NPs have been reported in literature, mainly focused on small particle sizes (<10 nm) prepared by microfluidic devices³⁶⁻³⁸ or in a tubular reactors³⁹ and syringe pumps⁴⁰ (semi-continuous): these papers deal with flow rates < 1 ml min⁻¹

¹, millimolar Ag concentrations and limited treated volumes, thus not suitable for a relatively large production (few g h⁻¹). An interesting experimental work is reported by Nishioka³⁸ and coworkers: Ag nanoparticles are produced in a tubular reactor heated in a microwave oven. The authors claim that by conventional heating in an oil bath, metal silver is deposited on the tubular reactor wall and the product quality deteriorates over time while by microwave heating the process is reliable over time. Similar fouling problems are reported by Lin and coworkers.⁴⁰

In this work we present the continuous polyol synthesis of AgNPs in the size range 10-120 nm using high precursor concentrations ($[Ag^+] \approx 0.12$ M in the reaction mixture). The reaction was carried out in the Segmented Flow Tubular Reactor (SFTR)⁴¹ heated in a conventional oil bath. A prominent feature in this experimental set-up is that an inert and immiscible solvent is introduced into the system and separates the reaction mixture into identical micro-volumes before transporting them into the reactor. This principle avoids back-mixing of the reaction mixture and creates identical conditions for the produced micro-volumes in terms of heat transfer and residence time within the reactor. Moreover, as already shown for several precipitation reactions^{42,43} and here presented for the first time for AgNPs production, the immiscible fluid protects the internal tubular wall reactor allowing long production time without product quality deterioration or fouling. In this paper the effects of the reaction temperature and the average molecular weight of PVP on the resulting particle size and distribution are investigated. The products were fully characterized by Transmission Electron Microscopy (TEM), high resolution X-ray Diffraction (XRD), Thermogravimetric Analysis (TGA), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Dynamic Light Scattering (DLS), Ultraviolet-Visible Spectroscopy (UV-Vis), and X-ray Disk Centrifuge Particle Size Analysis (Brookhaven Instrument, BI-XDC).

Synchrotron radiation was used both for X-ray diffraction (XRD) and for X-ray absorption spectroscopy (XAS). X-ray diffraction patterns were collected on dried powder as well as directly on the as prepared suspensions. X-ray Absorption Near Edge Spectroscopy (XANES) was used for the first time to directly measure the reaction yield.

Additionally, a correlation between the major plasmon peak in the UV-Vis spectra and the TEM particle size was identified. It is demonstrated that a series of relevant analytical data can be measured directly on the particle suspension. The combination of the applied analytical techniques allowed a growth mechanism to be proposed which can explain the experimental results obtained in the continuous production using the SFTR.

2. Experimental

2.1. Continuous Segmented Flow Tubular Reactor (SFTR)

A schematic view of the Continuous Segmented Flow Tubular Reactor (SFTR) is illustrated in Figure 1. More details are published elsewhere.⁴¹⁻⁴³ The SFTR is composed of a micromixer which ensures that the reactants are efficiently mixed, a segmenter, and a PTFE tubular reactor, placed in a thermostatic bath. Small suspension volumes (about 0.2 cm³) are thus created, producing microdroplets or microreactors in an immiscible fluid (*n*-dodecane, *n*-C₁₂), where the reaction – in this case Ag⁺ reduction and Ag precipitation – takes place. This small volume ensure a high homogeneity of the droplets and each of them is facing the identical *history* (e.g., residence time and heat exchange) throughout the tube.

Figure 1. Schematic illustration of the SFTR. The two reactants are introduced separately into the system and pass through various systems (micromixer, segmenter) in order to produce reaction microdroplets prior to going through the heated reactor where the formation of the particles occur.

The reaction or the precipitation occurs in the mixing chamber and/or induced by the rapid temperature change when the microreactors are heated in the thermostatic bath. According to fluid dynamic modelling, the temperature of the droplets reaches 95% and 99% of the bath temperature within 6 and 10 s, respectively.⁴⁴ Fouling on the inner tubular reactor wall is avoided due to the immiscible fluid by forming a thin film on the tube surface^{42,45} and thus allowing long continuous process times (>12 h). The residence time is determined by the pump flow rates and the tube length and adjusted according to the specific reaction kinetics. This is a steady-state process in which each step (mixing and reaction) is well separated, leading to a better control and reproducibility. If needed, after the tubular reactor, in the process line, a heat-exchanger can be

placed to cool down the reacting mixture and quench the reaction. Finally, a separation unit or decanter allows the separation of the product from the immiscible fluid; the product – particle in suspension – is collected, while the immiscible fluid is recycled in the process for environmental and cost concerns.

2.2. Polyol synthesis of silver nanoparticles in the SFTR

All chemicals were purchased from Sigma Aldrich and used as received. Ethylene glycol (EG) was distilled prior use. A modified procedure from Xia and co-workers was applied for AgNPs synthesis.⁴⁶ Two separate solutions of AgNO₃ (0.236 M) and PVP 10: $M_w = 10'000 \text{ g mol}^{-1}$ or PVP 40: $M_w = 40'000 \text{ g mol}^{-1}$ (2.16 M in terms of repeating units) were prepared. PVP and AgNO₃ were dissolved at 70 °C under sonication and at room temperature under magnetic stirring, respectively. In order to protect the AgNO₃ solution from sunlight, the container was shielded off by wrapping aluminium foil around it. The two reactants were introduced into the reactor system by pumping with two HPLC pumps at a rate of 1.5 ml/min. After forming the reaction mixture in the micromixer, the micro-volumes were made in the segmenter by passing through *n*-C₁₂ at a speed of 24.8 ml/min. In the experimental trial, the temperature range was kept between 120 and 150 °C. The residence time of the micro-volumes within the tube in the thermostatic bath was 12 min. In a second tubular section, the segmented suspension was cooled down. The silver sol was then collected in the decantation funnel and *n*-C₁₂ separated. The theoretical AgNPs production (100% yield) corresponds to 2.26 g AgNPs h⁻¹.

2.3. Product Characterization

Particles were characterized by TEM images (Philips CM30) measuring over 400 particles, DLS (Malvern Zetasized Nano ZS), BI-XDC (Brookhaven Instruments) and UV-Vis (Cary 50 Spectrophotometer).

TGA was carried out with a Mettler Toledo TGA/SDTA 851e in the temperature range 25-500 °C (heating rate 5 K min⁻¹). About 20 mg of Ag powders were treated in Ar/O₂ (20% O₂, 15 ml min⁻¹) atmosphere. A second run under reducing atmosphere Ar/H₂ (5% H₂, 10 ml min⁻¹) was carried out on selected samples.

Chemical analysis was carried out with an Agilent 7700x ICP-MS after digestion of the samples in HNO₃ and dilution in milliQ water, using external calibration standards.

XRD and XANES measurements were done at the Swiss Light Source (SLS, Paul Scherrer Institut, Villigen PSI, Switzerland). XRD were collected at the Material Science beam line (X04SA), at 25 KeV and using a 0.3 mm glass capillary.⁴⁷ Cell parameters were calculated by Rietveld refinement using the GSAS (General Structural Analysis Software)⁴⁸ and ICSD (Inorganic Crystal Structure Database).⁴⁹ Crystallite sizes (d_{XRD}) were estimated from the full path refinement using the GSAS (profile function #4).⁵⁰ Moreover, diffraction patterns were collected directly on the as prepared suspension, through a liquid cell sample holder with 10 mm of optical path.

In order to understand the influence of the key parameters on the precipitation process, the reaction yield (Y) needs to be measured. Y is defined as:

$$Y = \frac{Ag_n^o}{Ag_T}$$

where Ag_n^o and Ag_T are the amount of AgNPs obtained and the overall amount of silver in the system, respectively. Experimentally we notice that when the reaction is complete (Y=100%) the

as-prepared particle suspensions are stable over time with a shelf-time of several months. For $Y < 100\%$, silver mirror was formed over time on the storing vessel because of the reducing environment and the unreacted Ag^+ . Thus, the overall amount of silver is:

$$Ag_T = Ag_n^0 + Ag_m^0 + Ag^+$$

where Ag_m^0 and Ag^+ are metal silver deposited on the vessel as mirror and the unreacted silver ions, respectively.

The measurement of the reaction yield is not a trivial analytical problem to solve since: (i) it is not always possible to retrieve the solid quantitatively from the suspension; (ii) it is difficult to carry out chemical analysis on the supernatant because of the presence of residual particles in suspension; (iii) the chemical method, e.g. by titration with chlorine ions without AgNPs separation, may be affected by the nanoparticles interference. A different approach needs to be found out that (i) it is sensitive to the Ag^+/Ag^0 ratio, (ii) does not require solid-liquid separation, (iii) can be carried out on the liquid suspension just after the synthesis, ideally on-line, when $Ag_m^0 = 0$.

Here, a novel approach to measure the reaction yield by X-ray Absorption Near Edge Spectroscopy (XANES) is presented. XANES is a direct method to quantify the oxidation state of the absorbing atom. By fitting (Linear Combination Fitting, see later in this section), the relative amount of Ag^+ and Ag^0 can be calculated. Thus, when $Ag_m^0 = 0$, the reaction yield is calculated as

$$Y = \left(1 + \frac{Ag^+}{Ag_n^0}\right)^{-1} \quad (\text{Eq. 1})$$

In this paper, two Ag absorption edges were measured (K and L_3) and compared in terms of analytical results and experimental requirements.

The Ag L₃-edge XANES spectra were collected at the PHOENIX beamline (X07MA). The beamline was equipped with a Si(111) monochromator tuned to the Ag L₃-edge, assigned to 3351 eV using a thin Ag metal foil, also used as a standard for Ag⁰ specie. The experimental set-up closely follows the one reported in ref. [51]. The measurements were carried out in fluorescence mode, at room temperature in a 100 mbar He atmosphere. An appropriate sample concentration was chosen, in order to give the maximum contrast at the Ag-L₃ edge and minimize the over-absorption effects. Actually, the as-synthesized suspensions were used without dilution because preliminary tests demonstrate that over-absorption effects were negligible. To measure the incoming photon flux (I_0), a polyester foil (Goodfellow), coated with 50 nm of Ni, was put into the beam at the exit of the focusing optics, thus behind the last aperture before the sample. The total electron yield generated on the foil by the beam served as measure of I_0 .

The Ag-K edge XANES spectra were collected at the Super-XAS beamline (X10DA). The intensity of the incident beam (I_0) was measured with an argon filled ion chamber. The Ag⁺ standard and the sample suspensions were properly diluted in order to minimize hole-effects and then placed in 1 mm glass capillaries. X-ray absorption data from the sample were measured in transmission mode. A second argon filled ion chamber was used to measure I_1 . A thin sample of Ag metal foil was used for calibration and also as a standard for Ag⁰ specie. The calibration measurement was made with a third argon filled ion chamber (I_2) placed after I_1 . The position of the metal absorption edge (Ag, 25514 eV) could then be determined by placing the Ag metal standard between ion chambers I_1 and I_2 and measuring the absorption coefficient of the metal standard. In both XAS experiments a solution of Ag⁺, stabilized with HNO₃, was used as standard for Ag⁺ specie.

The XANES spectra were analysed by using the Linear Combination Fitting (LCF)⁵²⁻⁵⁵ option available in ATHENA.⁵⁶ With this method, the X-ray absorption spectrum is modelled by least squares fitting using linear combination of known species to fit the unknown spectrum. The underlying principle is the additive nature of the absorption from each species in the sample. The total absorption coefficient can be written as a sum of the chemical forms or species.

Mathematically, $Model = \sum_i f_i(STD_i)$ where *Model* is the least square fit to the sample spectrum over a selected energy range, and f_i is the scaling factors applied to each spectrum of the corresponding standard (STD_i) across the energy range of the fit. The scaling factors obtained from LCF represent the fraction of each standard species in the unknown sample. The LC fit has been carried out in the energy range 25400 – 25700 eV for the Ag-K edge and in the 3300 – 3450 eV range for the Ag-L₃ edge. The relative weights of the two reference standards (Ag^0 and Ag^+) are allowed to vary from 0 to 1, and the absorption edge energies, previously aligned, are kept fixed during the analysis.

3. Results

Following a single droplet within the tubular reactor, a clear colour evolution occurs over time, from colourless transparent to pale transparent yellow to deep red or dark suspensions. The colour change is due to the well-known localized surface plasmon resonance spectra that highly depend upon their size, shape, and surrounding environment. The transparent solution indicates that no reduction occurs during mixing at room temperature, while the reaction starts, induced by the temperature, in the thermostatic bath. The colour change is thus due to the Ag NPs nucleation and growth. Dark suspensions are obtained at high reaction yield and for rather large particle (>60 nm).

The collected products, in form of suspensions, were characterized both as suspension and as washed and dried powders.

Table 1 summarizes the synthesis condition and the average particle size of the 7 series of samples produced. The samples reported in Table 1 were collected for about 30 minutes of continuous production. At $T = 120\text{ }^{\circ}\text{C}$ and $\text{PVP} = 40\text{k}$, the reaction does not occur. It is worth nothing that, in the tested temperature conditions ($\leq 150\text{ }^{\circ}\text{C}$), if the process is carried out without PVP, the silver reduction does not occur.

Figure 2 shows representative TEM images of the samples G0, G1, G2, and G3 prepared with PVP 10k. The average particle size obtained ranged from 23(4), 25(4), 47(8) and 58(7) nm by conducting the experiments at temperature 120, 130, 140 and to 150 $^{\circ}\text{C}$, respectively. In the parenthesis is reported the measured standard deviation of the particle population, which evaluates the particle size distribution span. Figure 3 show the products (samples G4, G5 and G7) obtained when PVP 40 was used. The particle sizes was 7(2), 79(15) and 104(20) nm for temperature of 130, 140 and 150 $^{\circ}\text{C}$, respectively. The particle size distribution measured from the TEM images are also reported as inset (Figures 2 and 3).

Table 1. Summary of the *polyol synthesis* of AgNPs in the SFTR. In the parenthesis is reported the measured standard deviation of the particle population.

Sample name	Temperature (°C)	PVP M_w (g·mol ⁻¹)	TEM size (nm)	Mean diameter (nm)
G0	120	10k	23 (4)	14 (4)
G1	130	10k	25 (4)	20 (8)
G2	140	10k	47 (8)	33 (12)
G3	150	10k	58 (7)	56 (17)
G4	130	40k	7 (2)	9 (2)
G5	140	40k	79 (15)	107 (30)
G7	150	40k	104 (20)	123 (32)

Figure 2. AgNPs prepared with PVP 10k: (a) G0, (b) G1, (c) G2, and (d) G3.

Figure 3. AgNPs prepared with PVP 40k: (a) G4, (b) G5 and (c) G7.

After washed in ethanol, the surface plasmon bands in the visible region were measure by UV-Vis spectrometry. A bathochromic shift of the major plasmon peak λ_{max} from 402 to 453 nm as the average TEM diameter increases from 7 to 104 nm (see Figures 4-5) was observed. This correlation is shown in Figure 6. The position of λ_{max} depends on the solvent used for the measurements.⁵⁷

Despite the presence of a second broad plasmon peak for the sample with particles of 23 nm diameter, the DLS spectrum and TEM images did not provide the existence of two distinct particle populations. The shoulders evident on the UV-vis spectra of the sample G0 can be explained by the occurrence of non-spherical shapes within the particle population e.g. oblate spheroids. This effect is pronounced for small particle sizes, but vanishes at larger particle sizes due to the larger particle size distribution.⁵⁸

Figure 4. Particle size number distribution measured by DLS of the AgNPs prepared with the SFTR.

Figure 5. UV-vis spectra of the AgNPs prepared with the SFTR.

Figure 6. Correlation of the mean particle diameter (measured with TEM) with the position of the absorption maxima in the UV-vis spectra.

Figure 7. Particle size number distribution measured by DLS of the AgNPs prepared during the long term reaction (L1). Particles were analysed at different reaction times.

The synthesis reliability against time was conducted producing AgNPs for about 4 h at 150 °C using PVP 40k (sample L1, equivalent to sample G7). These synthesis conditions have been selected because complete reduction to Ag^0 was obtained (see later in this section). Suspension aliquots were taken at regular times and DLS particle size distributions recorded. Figure 7 shows the overlapping particle size distributions and Table 2 shows the percentile diameters d_{n10} , d_{n50} and d_{n90} against time. The mean particle diameter of the collective samples (all L1 aliquots) was measured by DLS, by TEM image, as well as by BI-XDC. Results are summarized in Table 3.

Table 2. Percentile Diameters measured with DLS for AgNPs (L1) prepared at 150 °C running over 4 hours.

Aliquot taken after reaction time (min)	d_{n10} (nm)	d_{n50} (nm)	d_{n90} (nm)	Mean diameter ^a (nm)
15	73	99	146	110 (27)
30	76	104	154	112 (29)
60	69	96	146	104 (30)
120	71	95	139	105 (25)
180	76	104	152	106 (30)
240	72	98	147	101 (30)

^aMean numerical diameter. In the parenthesis is reported the measured standard deviation of the particle population.

Table 3. Mean diameter for AgNPs (L1) prepared at 150 °C running over 4 hours. In the parenthesis is reported the measured standard deviation of the particle population.

	DLS d_{n50} (nm)	TEM (nm)	XDC (nm)
Particle size	100 (30)	87 (17)	91 (26)

The reaction yield was determined on selected samples by XANES spectroscopy. Both the Ag L₃-edge and K-edge XANES spectra have been collected. The normalized $\mu(E)$ data obtained for the two Ag species (Ag⁺ and Ag⁰) were linearly combined to fit the normalized $\mu(E)$ data of selected samples using the Linear Combination Fitting (LCF) method.⁴⁹⁻⁵² The low energy of the Ag-L₃ edge (3351 eV) allows reducing the radiation damage on the samples during the

measurements, but the interference from other edges (i.e. Ag-L₂ at 3524 eV) cannot be excluded, limiting the energy range in which the samples can be measured. Moreover, the low energy of the Ag-L₃ edge challenges the measurement from the point of view of the experimental set-up and materials needed for the optical windows. For these reasons, on selected samples, Ag-K edge (25514 eV) XANES spectra have been collected as well. In this case, because of the higher energy used, the beam damage is more probable, but the measurement can be much faster and the experimental setup as simple as a standard glass capillary.

The percentage of Ag⁺ and Ag⁰, the corresponding errors, the goodness-of-fit (*R*-factor, i.e. a measure of mean square sum of the misfit at each data point), the calculated yield, and the gravimetric yield, measured weighting the collected product after 3 consecutive washing and centrifugation cycles, is reported in Table 4. The reported incertitude on the measurement is obtained from the ATHENA software and refers to the error on the LCF. Sample G7 and L1 are completely converted to Ag⁰ and the fitting is actually not necessary because their XANES spectra overlap the Ag metal standard. It is worth nothing that the incertitude of the measurement technique has to be experimentally evaluated by *ad-hoc* trials. For the time being, based on our experience and the literature⁵⁹⁻⁶¹, the measurement incertitude can be estimate below 3%.

As example, Figures 8 reports the normalized of Ag L₃-edge and K-edge XANES spectra for the sample G3 and G4, respectively. The goodness-of-fit can also be seen from the little difference (plotted as green line) between the experimental and LC fitted data.

(a)

(b)

Figure 8. Example of LC fit for (a) Sample G3 (Ag-L₃) and (b) Sample G4 (Ag-K) edge XANES spectrum. Circles: experimental data; Red line: LC fit; Blue line: fraction of Ag⁺ making up the fit; Pink line: fraction of Ag⁰ making up the fit; Green line: Difference between experimental data and LC fit.

Table 4. Summary of the amount of Ag⁺ and Ag⁰ of selected samples determined by XANES spectroscopy (L₃-edge or K-edge). The yield is determined by Eq. 1.

	Ag ⁰ (%)	Ag ⁺ (%)	R-factor (%)*	Yield XANES (%)	Yield gravimetric (%)
G3 (L ₃ -edge)	74 ± 1	25 ± 1	0.002	75 ± 2	73 ± 5
G4 (K-edge)	57 ± 2	41 ± 2	0.006	58 ± 4	<i>n.d.</i>
G5 (K-edge)	92 ± 1	5 ± 1	0.002	95 ± 2	89 ± 5
G5 (L ₃ -edge)	93 ± 1	6 ± 1	0.002	94 ± 2	89 ± 5
G7 (L ₃ -edge)	>97	-	-	>97	95 ± 5
L1 (L ₃ -edge)	>97	-	-	>97	95 ± 5

* defined as
$$R = \frac{\sum (XANES_{measured} - XANES_{calculated})^2}{\sum (XANES_{measured})^2} \times 100$$

Table 4 reports the yield measured by gravimetric method. In this case the product needs to be washed and retrieved by centrifuging at least three times. This procedure was not possible for sample G4 because of the small particle size. The gravimetric yields are in good agreement with the XANES values, considering that a fraction of NPs can be lost during the washing and centrifugation treatments.

The purity of selected solid samples, after centrifugation, washing, and drying were analysed by ICP-MS and TGA. The chemical analysis carried out on samples G3 and G7 showed no relevant contaminants ($\text{Fe} \approx 20$ ppm; $\text{Na} \approx 5$ ppm; Ni , Zn , $\text{Mo} \approx 2$ ppm) and the Ag content were about 90% and 97%, respectively. These results are coherent with the TGA experiments which show that the weight loss against temperature (Figure 9) may be attributed to organic residuals on the particle surface. The organics are completely burned out at about 280 °C for samples L1 and G7. Sample G3 shows a different behaviour with a clear two-step weight loss. The reason of the second weight loss, which is completed at 500 °C, is under investigation, but could be ascribed to the lower molecular weight of PVP used in the synthesis.

A subsequent thermal treatment under reducing conditions (5% H_2 , balance Ar) up to 500 °C (not shown) was performed. The absence of weight changes confirm that the samples were not oxidized due to the thermal treatment carried out in air.

Figure 9. TGA measurements conducted on the recovered powders from samples G3, G7 and L1.

High resolution XRD patterns on powders were collected on selected samples (G3, G4, G5, G7). As example, Figure 10 shows the powder diffraction pattern for sample G7. Organic residues, in agreement with the TGA experiments, gave a relevant background contribution. The best fit obtained by Rietveld refinement suggests the presence of two populations of crystallites of about 10 nm and 80 nm. The calculated crystallite size is smaller than the TEM particle size but in agreement with the multi-domain substructure of the particles (Figures 2, 3). The diffraction patterns do not show any crystalline secondary phases. Figure 10 shows the diffraction patterns collected on the as prepared suspensions (G3, G4, G5) as well. In these cases, the peak broadening is a complex convolution of particle size and the liquid suspension thickness under analysis but the collected patterns show good signal-to-noise ratio. It can be seen that sample G4 has no diffraction peaks because the particles are both small (7 nm) and few (low

conversion yield), while G3 and G5 (and G7, not showed) gave excellent signals. Again, no secondary phases were detected.

Figure 10. Diffraction patterns collected on powder (G7) or on the as prepared suspension (G3, G4, G5) after background subtraction.

4. Discussion

Due to the evident colour change during the reaction progress (due the surface plasmon effect which strongly depends on the Ag^0 particle size), the drop-to-drop homogeneity can be easily verified along the tubular reactor. The constant and reproducible colour of the droplets is a clear demonstration of the system stability. However, in some cases, for instance when a small gas bubble was dosed by one pump at the beginning of an experimental trial, a droplet of different colour was immediately recognized in the tube due the chemical difference of that droplet with respect to the neighbours' droplets.

The powders produced over 4 h shows constant particle size distribution, demonstrating that the preparation of AgNPs can be extended for a long production time with constant product properties.

Thermogravimetric measurements and chemical analysis gave coherent results: the product consists of pure Ag and organic residues (about 3 wt%), most probably PVP on the particles surface. The organic residues are burned out at about 250 °C. The overall metallic contaminants concentration is below 50 ppm.

The particle size distributions of the produced samples were measured by several techniques and a general good agreement among the measurements were demonstrated. We can conclude the most convenient method is DLS because (i) limited amount of product is needed, (ii) it is fast and (iii) inexpensive, and (iv) reliable results are obtained. The major drawback is that DLS is an offline method. Nevertheless, the correlation between TEM size and UV-Vis spectroscopy (Figure 6) open the possibility to monitor particle size on-line using UV-Vis spectroscopy.

The AgNP_s conversion yield was measured from XANES spectra using both K and L₃-edges, giving comparable results (Sample G5, Table 4). The higher energy of the K-edge greatly

simplifies the experimental set-up and the feasibility of the direct measurement of the reaction yield on the suspension was demonstrated (Figure 8). Similarly, X-ray diffraction patterns of the powder may be efficiently measured from the suspension with a liquid sample holder cell, as demonstrated in Figure 10. It turns out that these investigations may be carried out directly on the as prepared suspension, ideally *in-situ* in the SFTR reactor. In principle, the most relevant particle formation parameters such as primary particle size by XRD (the crystallite size), secondary particle size by UV-Vis spectroscopy (thanks to correlation with the TEM size) the particles, and conversion yield by XANES might be studied *in-situ* and time-resolved, allowing the detailed kinetic study of particle formation.

As shown in Table 1, average particle diameter can be tuned by changing the reaction temperature and the PVP average molecular weight. The effect of the temperature has also a relevant influence on the conversion yield and size: higher temperatures gave higher yields and bigger particle sizes. Moreover, the particle size distribution span remains almost unchanged against yield.

Such behaviour may be explained by a two stage process where nucleation and growth occur on two different times scale. It is plausible to consider that particle nucleation occurs only in a limited time frame at the beginning of the precipitation – which visually corresponds to the time frame from colourless solution to pale yellow suspension – producing a defined number of small particles. Then, this population of particles grow over time, consuming Ag^+ ions, confirming that reduction to Ag^0 occurs. The reducing agent is the *in-situ* generated glycolaldehyde formed by oxidation of EG at elevated temperatures. It should be mentioned here, that this oxidation process is strongly accelerated by the temperature⁶². For this reason, at 130 °C and 12 min of

reaction time, the conversion yield is very low while at 150 °C the reaction is quantitative for the same reaction time.

Nucleation could be controlled by PVP.⁶³ This hypothesis is supported by the fact that (i) tests carried out without PVP resulted with no precipitation of AgNPs at all, (ii) it is known that PVP acts both as stabilizer and reductant,⁶⁴ and (iii) the particle size decreases with PVP molecular weight. Commercially available PVP are commonly terminated with hydroxyl (-OH) end-groups⁶⁵. These terminal groups act as reducing agent: keeping constant the ratio between polymer repetition unit and silver, the number of terminal groups increases for shorter polymer backbone, i.e., PVP 10k has more hydroxyl groups compared to PVP 40k. Thus, provided that the particles can grow (i.e., the temperature is high enough) PVP 10k can produce more nuclei, (i.e., smaller particles) than PVP 40k.

We conclude that our experimental results are coherent with a two sub-sequent steps: (i) nucleation, which is controlled by the amount of PVP terminal groups and (ii) particle growth, which is tuned by the temperature through its influence on the EG reduction potential. In order to consolidate these findings a detailed experimental trial on precipitation kinetics is currently in progress.

5. Conclusions

A novel method to prepare AgNPs in a continuous way has been presented. Here, the segmented flow kept in the reactor provides optimization beyond to state-of-the-art of continuous synthesis methods by creating more homogenous reaction conditions. The variation of the reaction temperature and the average molecular weight of the PVP lead to the systematic change in the average particle sizes and reaction yield. Our experimental data suggest that PVP is controlling the nucleation step while particle growth is tuned by the temperature through its influence on the EG reduction potential.

Particle size and reaction yield data have been combined in order to outline a rational (nucleation and growth) formation path. The method to measure the reaction yield was one of the most relevant achievements of this experimental work. Yield was measured directly in the produced particle suspension by linear fit of XANES spectra. Synchrotron-light diffraction patterns were also collected from the suspension. Moreover, a clear correlation between TEM size and the major plasmon peak of the UV-Vis spectra has been identified. We have demonstrated that key parameters such as primary particle size, secondary particle size, and conversion yield may be investigate *in-situ* and time-resolved. Thus, a comprehensive particle formation mechanism can be investigated.

Finally, the potential of the SFTR to prepare high amounts of AgNPs over a long period was demonstrated by running the reaction for 4 h, obtaining constant particle size distribution with production rate $> 2 \text{ g h}^{-1}$.

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Supporting Information Available: Experimental details and characterizations of the AgNPs prepared by batch type reactions with varying reaction volumes. This information is free of charge via the Internet at <http://pubs.acs.org>.

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