Transforming nano-science to nano-technology: Manipulating the size, shape, surface morphology, agglomeration, phases and defects of silver nano-particles under continuous flow conditions

K. Swaminathan Iyer*, C. L. Raston** and M. Saunders***

* Centre for Strategic Nano-fabrication, School of Biomedical, Biomolecular and Chemical Sciences, The University of Western Australia, Crawley, WA-6009, Australia, siyer@cyllene.uwa.edu.au.

** Centre for Strategic Nano-fabrication, School of Biomedical, Biomolecular and Chemical Sciences, The University of Western Australia, Crawley, WA-6009, Australia, clraston@chem.uwa.edu.au.

*** Centre for Microscopy, Characterisation and Analysis, The University of Western Australia, Crawley, WA-6009, Australia, martin@cmm.uwa.edu.au.

ABSTRACT

Spinning disc processing (SDP) is an instantaneously scalable, continuous flow and high throughput flash nano-fabrication technology which embraces green chemistry metrics. It has been used to prepare silver nano-particles with remarkable control in size (5 – 200 nm), shape, surface characteristics, and phase (cubic versus hexagonal), along with imparting defects for particles > 10 nm diameters. The control is associated with changing the nature of the stabilising surfactant, the concentration of the reactants, flow rates, temperature and the nature of the rotating surface.

Keywords: Spinning Disc Processor (SDP), Green chemistry, Continuous flow processing, Silver nano-fabrication, Process Intensification.

1 INTRODUCTION

A growing demand for the fabrication of electronic components, optical detectors and biochemical sensors with nano-dimensions has initiated several theoretical and experimental investigations in the field of nanotechnology. Advancement in technology demands synthesis of nano-particles with controlled size, shape and structure for a broad range of applications such as diagnosis and monitoring of diseases, drug delivery, proteomics and the environmental detection of biological agents [1].

Noble metal nano-particles comprise a fundamentally interesting class of matter because of an apparent dichotomy between their sizes and many of their physical and chemical properties [2]. Silver particles reduced to nanometer dimensions are of particular interest because they exhibit unique optical properties in the visible spectral range due to the excitation of the collective oscillations of conducting electrons known as plasmon resonance or surface plasmons [3,4]. Near-IR region light penetrates the body with negligible absorption from tissue, photons from that spectral region could be used to focus thermal energy in regions of the body where the nano-particles are concentrated; at the same time, photon scattering from these nano-particles can be used in imaging during the radiolysis treatment.

In the midst of mounting concerns pertaining to nano-toxicology in developing novel applications, the US Environmental Protection Agency (EPA) has been strongly advocating "green" nano-technology to academia, industries and other government agencies [5]. Consequently there is growing need to develop an expedient technology that is not only scalable but also offers precise control over the particle size, shape and surface properties.

Herein we report the synthesis of silver nano-particles using spinning disc processing (SDP) technology, Figure 1.

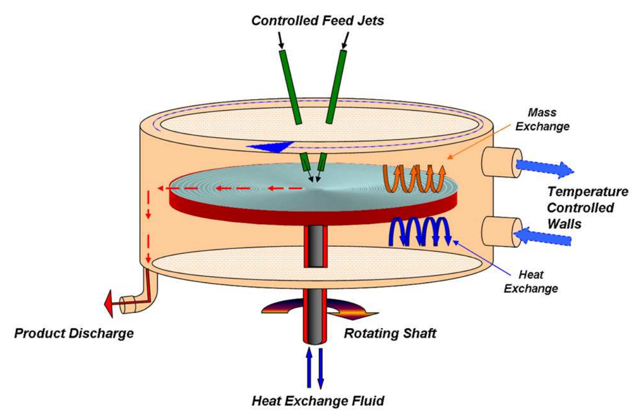


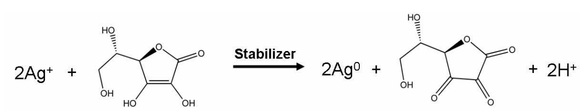
Figure 1: Schematic of a Spinning Disc Processor.

Apart from being a scalable continuous flow process, SDP has the potential to instantaneously (no time dependence) control the particle size, shape, agglomeration and surface characteristics with utmost efficiency thereby affording particles of narrow size distribution. The key components of SDP includes: (i) a 100 mm rotating disc with controllable speed, and (ii) feed jets located at a radial distance of 5 mm from the center of the disc. SDP generates a very thin fluid film (1 to 200 μm) on a rapidly rotating disc surface (300 to 3000 rpm), within which nano-particle formation occurs, Figure 1. The thinness contributes to many influential chemical processing characteristics, one being a very high surface area to volume ratio, resulting in more favorable interactions between the film and its surroundings.

2 EXPERIMENTAL

High purity analytical grade silver nitrate (Unilab), L-ascorbic acid (Chem-Supply), soluble starch (Univar), PEG-400 and poly(4-vinylpyridine) (P-4PV) (MW-60,000) (Sigma-Aldrich) were used as obtained. Water with a resistivity greater than 18 MΩ.cm was acquired from a Millipure Milli-Q system. Starch solution (0.03 wt%) was used to make stock solutions of silver nitrate and ascorbic acid of varying concentration (12 mM – 30 mM). Various concentrations were screened and the optimal experimental conditions are reported. A spinning disc reactor 100 series (Protensive, Inc) was used. Integrated feed pumps were used to feed (0.5 ml/s) the reactants on the rotating disc. The product was collected from the reactor for analysis. The optical properties of the silver nano-particles were monitored using a Perkin-Elmer UV-Vis spectrophotometer. The size and the morphology were examined by transmission electron microscopy (TEM JEOL 3000F and JEOL 2000). ATR-FTIR analysis was performed using a Scimitar series, Varian Inc, spectrometer.

The synthetic method herein is based on the reduction of silver nitrate by an environmentally benign agent ascorbic acid (vitamin C) in water (Scheme 1), with nontoxic material soluble starch (A), PEG (B) and P-4VP(C) as stabilizing agents.



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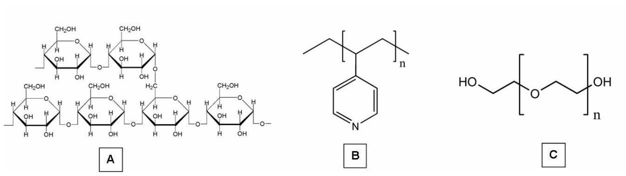

3 RESULTS AND DISCUSSION

The size of the silver nano-particles was varied from 5 nm up to 200 nm by carefully adjusting the concentration of the feed and/or regulating the disc speed, Figure 2. At high disc speeds strong shearing forces result in thin layering of the reagent solution which permits uniform heat transfer and homogenous concentration fields throughout the entire reaction mixture. Consequently, after nucleation all the particles will have a very similar growing condition which is of paramount importance for producing nano-particles with narrow size distributions (smaller standard deviation). As the disc speed is lowered the concentration and temperature fields become less uniform and the driving force for Ostwald ripening becomes more dominant resulting in a broad size distribution of nano-particles (larger standard deviation).Lower concentration feed on the disc may be ideally used at lower disc speeds to overcome the Ostwald ripening obstacle.

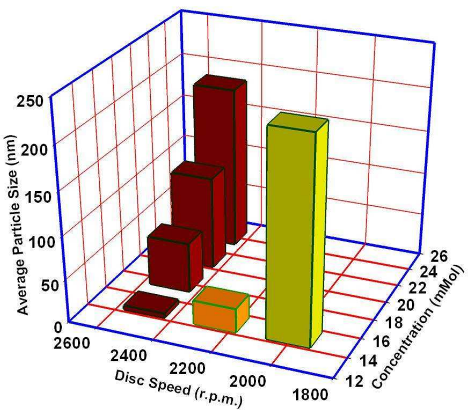

Figure 2: Average particle size distribution as a function of disc speed and feed concentration.

Concentration can be a limiting parameter in certain nano-fabrication protocols due to high toxicity of the reagents or the cost of the precursors, while the end application may desire larger nano-particles. It is therefore very important to incorporate operational flexibility that enables synthesis of nano-particles of larger size even when the precursor concentration is low. Additionally for certain reaction kinetics it is essential that the disc is operated at lower speeds to ensure completion without being hindered by the Ostwald ripening effect. SDP technology offers the flexibility of varying the nano-particle size at low feed concentrations on a "smooth" disc with corresponding lower levels of micro-mixing when compared to a "grooved" disc (Figure 3).

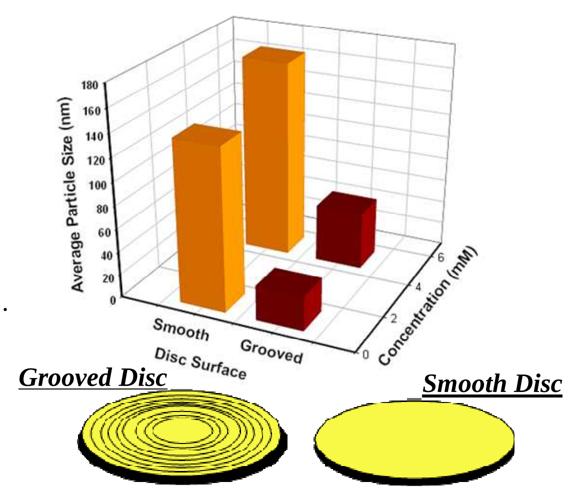

Figure 3: Particle size distribution for different discs.

A narrow particle size distribution was achieved using a grooved disc surface, while the use of a smooth disc surface resulted in a broader size distribution. The corrugated nature of grooved disc promotes shear induced micro-mixing of the thin fluid film on the disc [6]. Efficient micro-mixing is of paramount importance to ensure that all the particles are exposed to the same conditions to maintain a narrow size distribution. unlike on a smooth disc. By using surface roughening, the wetting of the disc surface can be increased compared to a smooth disc surface. Non-uniform wetting of the disc, results in dry spots and formation of rivulets which significantly reduce the transport rates achieved on the disc. However, one of the ways of overcoming these obstacle is using a slightly elevated disc temperature on the smooth disc. The thin film is subjected to flash heating on the disc and rapid cooling on the walls. The flash heating instantaneously enhances the mass and heat transport rates, thereby promoting convective micro-mixing. Indeed the increase in temperature resulted in smaller particles with a very narrow size distribution (Figure 4).

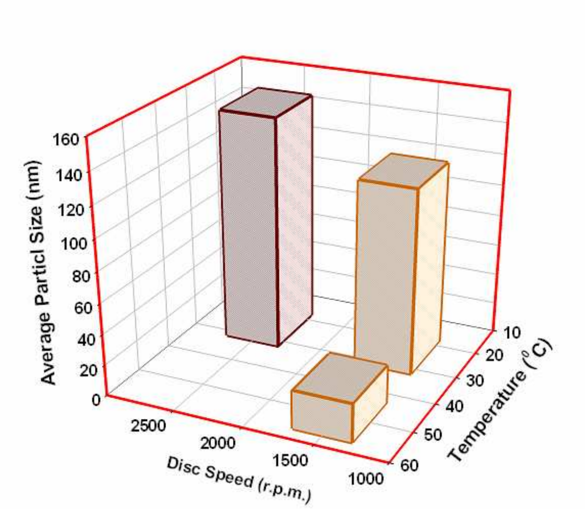

Figure 4: Particle size distribution on a smooth disc at different temperature.

TEM analysis of the silver nano-particles (Figure 5A and 5B) indicated that the larger nano-particles existed in the cubic phase, and were associated with strain effects and defects. The the smaller nano-particles (< 10 nm) preferred the hexagonal phase and were essentially defect free. Substituting starch as a capping agent with readily available P-4VP and PEG-400, resulted in instantaneously changing the particle shape and dimension from spheroidal (starch) to acicular (PEG-400) and rosette (P-4VP) nano-structures (Figure 5C and 5D). Similarly the length/diameter of the acicular particles and structure of the rosette nano-particles can be readily changed by varying the concentration of the reagents, molecular weight of PEG/P-4VP and the speed of the disc at room temperature.

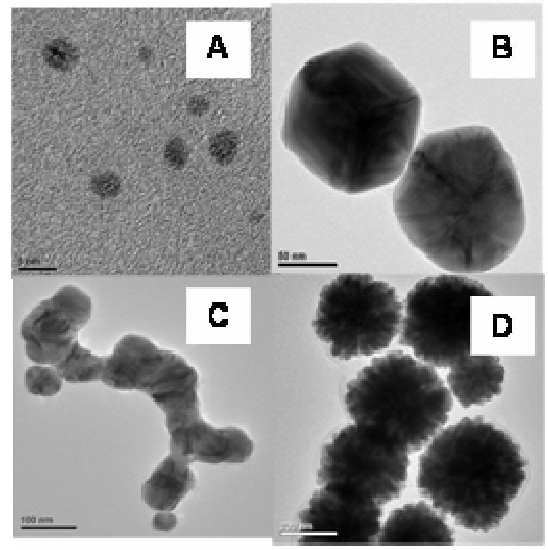

Figure 5: TEM of silver nano-particles stabilized by starch (A &B), PEG (C) and PVP (D).

4 CONCLUSION

We have developed a novel scalable method for the synthesis of silver nano-particles using spinning disc processing, as *a continuous flow reactor*, to manipulate the size, shape, morphology, defects and phases of the nano-particles instantaneously. It is a rapid thoughput, flash nano-fabrication approach which is amenable to combinatorial techniques, and we believe it will be applicable to the synthesis of a wide range of other nano-materials. SDP is a paradigm shift in developing nano-technologies which can address nano-toxicology issues, scalability, effluent treatment and hazardous work environment at the conception stage rather than attempting to make a new process or product scalable and non-toxic after its development.

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