Advanced Powder Technology xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Formation mechanisms for gold nanoparticles in a redesigned Ultrasonic Spray Pyrolysis

Peter Majerič [a,*], Darja Jenko [b], Bernd Friedrich [c], Rebeka Rudolf [a,d]

[a] University of Maribor, Faculty of Mechanical Engineering, Smetanova ulica 17, 2000 Maribor, Slovenia
[b] Institute of Metals and Technology, IMT, Lepi pot 11, 1000 Ljubljana, Slovenia
[c] IME Institute of Process Metallurgy and Metal Recycling, RWTH Aachen, Intzestraße 3, 52056 Aachen, Germany
[d] Zlatarna Celje d.d., Kersnikova 19, 3000 Celje, Slovenia

ARTICLE INFO

Article history:
Received 26 July 2016
Received in revised form 28 November 2016
Accepted 13 December 2016
Available online xxxx

Keywords:
Ultrasonic Spray Pyrolysis (USP)
Influential synthesis parameters
Formation mechanisms
Gold nanoparticles
Transmission Electron Microscopy (TEM)

ABSTRACT

The aim of this article was an explanation of the gold nanoparticle (AuNP) formation mechanisms which take place in a redesigned Ultrasonic Spray Pyrolysis (USP). Depending on the synthesis parameters of gold concentration in the precursor solution, gas flow and reaction temperature, we have previously obtained a combination of spherical, irregular and cylindrical AuNPs. Two parameters (gold concentration and gas flow) were determined to be the most influential on the shapes and sizes of the produced AuNPs. The effects of these two influential synthesis parameters were evaluated on controlling the formation mechanisms: Gold concentration (2.5 and 0.5 g/l Au) in the precursor solution of $HAuCl_4$ dissolved in water and gas flows of (i) aerosol carrier gas N_2 (1.5, 3.0 and 4.5 l/min) and (ii) reduction gas H_2 (1.0, 1.5 and 2.0 l/min). Depending on the parameter conditions, the AuNPs are formed from a combination of the liquid/solid phase (Droplet-to-Particle mechanism, DTP), the gas phase (Gas-to-Particle mechanism, GTP) and from intermediate secondary droplets, formed from primary droplet explosions. Increasing the gas flow affected the evaporation of the solvent (water) and diffusion of the solute ($[AuCl_4]^-$) in the aerosol droplets, which resulted in the formation of more uniformly shaped AuNPs and with narrower size distributions than before. With favorable parameter conditions increased control over AuNP synthesis with USP has been achieved.

1. Introduction

Spray pyrolysis is a known method for synthesis of fine powders and nanoparticles, capable of synthesizing spherical, hollow, core-shell, porous and other structures, of various materials such as metals and ceramics, with high elemental and phase purity [1–5]. Even though this is a relatively known process of powder production of a wide selection of materials, the specifics for nanoparticle formation are not known for a lot of them.

Gold nanoparticles (AuNPs[1]), along with silver and copper, are the most common nanoparticles used to obtain the surface plasmon effect [6]. The AuNPs' unique properties make them useful in the fields of Biotechnology, Energy, Chemistry and Information Technology [1,7], while the main current markets for AuNPs are in Biomedicine, in tissue or tumor imaging, drug delivery, photothermal therapy and immunochromatographic identification of pathogens in clinical specimens [8,9]. The physical and chemical properties of AuNPs are determined by their size, morphology, surface structure and purity. Although there are several methods for producing AuNPs, controlling their synthesis with a uniform size and morphology still remains a challenge. Several studies have been devoted to accomplish this [6,7,10–13]. Generally, the synthesis of AuNPs involves the Sodium Citrate reduction method, phase transfer method, templating method, seed-mediated method or chemical radiation. Synthesis via aerosol routes like Ultrasonic Spray Pyrolysis (USP[2]) enables production of various nanoscaled materials, including gold. It is relatively simple, flexible and can also be used for film processing. Control of nanoparticle properties can be achieved with careful selection and modification of the USP process parameters [4,5].

With USP, nanoparticles are synthesized from micron-sized droplets of a starting solution. These are created via atomization

* Corresponding author. Fax: +386 2 220 7990.
E-mail addresses: peter.majeric@um.si (P. Majerič), darja.jenko@imt.si (D. Jenko), bfriedrich@ime-aachen.de (B. Friedrich), rebeka.rudolf@um.si (R. Rudolf).

[1] AuNPs – gold nanoparticles.

[2] USP – Ultrasonic Spray Pyrolysis.

http://dx.doi.org/10.1016/j.apt.2016.12.013
0921-8831/

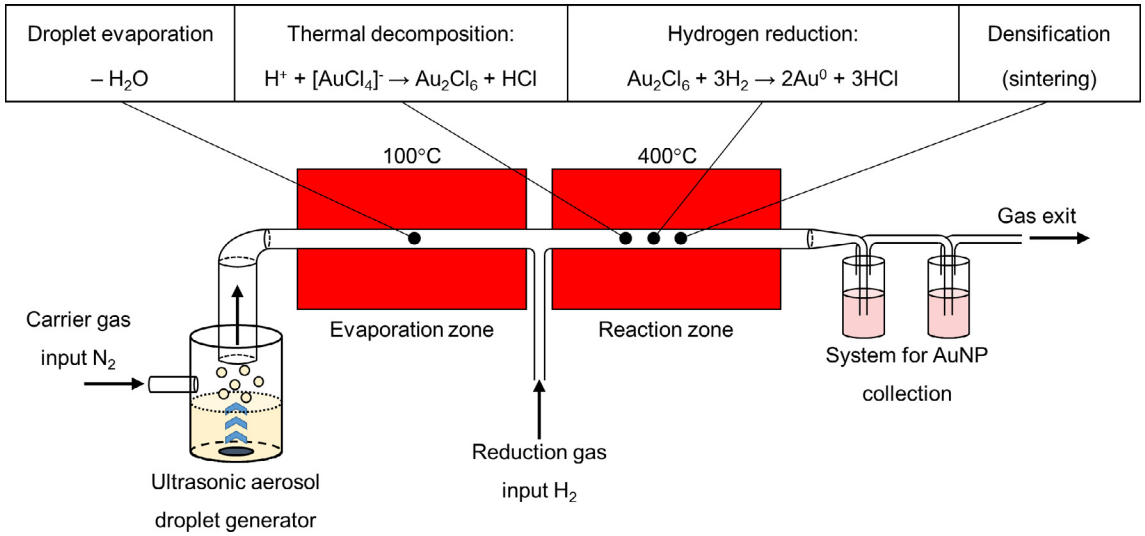

Fig. 1. Modular redesign of USP.

with ultrasound. After the droplets are created they begin to evaporate immediately [14]. After evaporation, a dried nanoparticle is left, which needs to be decomposed or otherwise altered chemically with reduction or oxidation. The final nanoparticle is then formed and collected in a suitable form, as a dried powder, or in a suspension in a suitable medium. These mediums are used to prevent further reactions, such as oxidation, or to stabilize the nanoparticles and prevent agglomeration, where stabilizing agents, such as Sodium Citrate, can be used. The final nanoparticle size is affected heavily by the solids concentration in dilute solutions (1–5 wt.%), but remains roughly unchanged in more concentrated solutions [14]. There are two formation routes which are generally seen in spray pyrolysis: Droplet-to-Particle (DTP[3]) and Gas-to-Particle (GTP[4]) [4,5,15]. In DTP, a single nanoparticle is formed from a single aerosol droplet via evaporation and chemical reactions (decomposition, reduction, or oxidation). In GTP, nanoparticles are formed from the gaseous phase, with formation of new nuclei and several nanoparticles in sizes from a few nm to a few 10 nm are formed from a single aerosol droplet.

As the main synthesis steps in USP are droplet evaporation, precursor conversion and nanoparticle formation, the redesign was done in order to provide more control over the aerosol droplet evaporation and solvent diffusion inside the droplet, for the formation of nanoparticles with a more uniform shape. It is postulated, that the droplet evaporation has the most influence on determining the shape of the final nanoparticles [3,16] and can produce solid, hollow or other shapes of nanoparticles [17]. Several experiments were done in order to determine the AuNP formation mechanisms in the modular redesign of the USP [18,19], Fig. 1.

Previously, we have reported a bimodal size distribution obtained by the redesigned USP system [19]. In order to determine the formation mechanisms, the experiments on the redesigned USP were carried out with changing only the parameters of Au concentration in the precursor and temperature in the evaporation zone. We have ascertained that the bimodal distribution was due to GTP and DTP mechanisms occurring simultaneously in the USP process, when synthesizing AuNPs from $HAuCl_4$. The redesigned USP improved the morphologies of AuNPs compared to the conventional USP, as mainly spherical and some irregular nanoparticle shapes were produced. However, a bimodal size AuNPs' distribution and both formation mechanisms were always present. In order to eliminate bimodal size distribution, the effect of one of these mechanisms needs to be minimized.

In this paper, control of the formation mechanisms of AuNP synthesis with USP was approached by changing the parameters of the precursor Au concentration and gas flows. Based on previous rsearch, it was determined, that the reaction temperature in the range from 300 to 500 °C has a lesser influence on the shapes and sizes of the produced AuNPs in our USP system. It was seen that higher temperatures significantly increase agglomeration. For this reason, the reaction temperature should be kept below 500 °C. The parameter values were selected based on previous experience [19] in order to produce AuNPs of a few 10 nm in size.

2. Materials and methods (experimental)

The synthesis of AuNPs was carried out on the redesigned USP equipment at the IME Institute of Process Metallurgy and Metal Recycling, RWTH Aachen, Germany [18,19], Fig. 1. Precursor solutions of Au were prepared with dissolving hydrogen tetrachloroaurate ($HAuCl_4$, ~50% Au basis, Sigma-Aldrich) in deionized (DI) water. The concentrations of Au in the precursor solutions were 0.5 and 2.5 g/l (0.05 and 0.25 wt.% respectively). The prepared solutions were put into the Ultrasonic Aerosol Generator (Gapusol, RBI France, piezoelectric transducer membrane frequency 2.5 MHz), where they were subjected to an ultrasound to produce aerosol droplets of diameters ranging from 1 to 15 µm, with an average size of 5–6 µm [20]. The aerosol was transported to the heating zones with N_2 gas through quartz glass tubes of 2 cm diameter. Hydrogen gas was added for reduction of gold chloride to pure gold metal nanoparticles. The first heating zone, used for droplet evaporation, was set at a temperature of 100 °C whereas the second heating zone was set at a temperature of 400 °C and was used for reactions required for obtaining pure AuNPs (the length of each heating zone was 28 cm). To determine the gas effects on the synthesized nanoparticles' sizes, three gas flows were used (low: 1.5 l/min N_2 + 1.0 l/min H_2, medium: 3.0 l/min N_2 + 1.5 l/min H_2 and high: 4.5 l/min N_2 + 2.0 l/min H_2). Table 1 shows the experiments performed.

The nanoparticles were collected in 0.1% solution of Na-citrate with DI water for stabilization purposes [21]. No subsequent use and testing of the produced nanoparticles were intended, for instance biocompatibility testing, for which different stabilizing

[3] DTP – Droplet To Particle.
[4] GTP – Gas To Particle.

Please cite this article in press as: P. Majerič et al., Formation mechanisms for gold nanoparticles in a redesigned Ultrasonic Spray Pyrolysis, Advanced Powder Technology (2017), http://dx.doi.org/10.1016/j.apt.2016.12.013