Silica-coated Ag nanoparticles by scalable flame technology

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ABSTRACT

Silver (Ag) nanoparticles dispersed in an amorphous silica (SiO_2) matrix or coated by a SiO_2 layer were synthesized by flame spray pyrolysis (FSP). The coated nanoparticles were produced by using a modified enclosed FSP setup, in which the SiO_2 precursor was injected through a ring above the FSP nozzle at various burner-ring-distances (BRDs), after the core Ag nanoparticles had been formed. The produced nanoparticles were characterized by XRD, BET, TEM and UV/vis analysis. The Ag particle size was possible to be controlled by tuning the FSP parameters. For the SiO_2 coated nanoparticles, larger Ag core sizes were obtained for higher BRDs. All the produced nanoparticles exhibited the characteristic plasmon resonance frequency of Ag nanoparticles.

Keywords: silver, silica, nanoparticles, coating

1 INTRODUCTION

Silver (Ag) nanoparticles play an important role in photography, catalysis, biological labeling, photonics, optoelectronics and surface enhanced Raman scattering [1]. This is attributed to the unique optical properties of Ag that originate from the collective oscillations of conduction electrons, termed as surface plasmon polariton resonances [2]. This intrinsic property of Ag nanoparticles is mainly determined by their size, shape, composition, crystallinity, and structure. In principle, one could control any one of these parameters to fine-tune the corresponding optical properties. An attractive way to do this is by tuning the dielectric medium which surrounds them [3]. Such a dielectric medium is silica (SiO_2), with which the unique shape- and size-dependent optical properties of Ag nanoparticles can be tailored.

Coating Ag with SiO_2 can also enhance the stability of Ag nanoparticles and provide tunable solubility in various solvents [4]. Monodispersed SiO_2-coated Ag particles readily self-assemble into photonic crystals with an optical band gap in the visible region [5]. Moreover, SiO_2 shells can be easily functionalized, allowing the nanoparticles to be conjugated to other substrates or molecules, a property extremely useful in bio-labeling [6].

There have been reported various wet techniques to encapsulate fine metal nanoparticles, such as Ag, in a SiO_2 shell. These methods are effective but time-consuming and difficult to control [4]. Additionally, most of these methods can only be used for coating large metallic particles (~50 nm in diameter) because small particles are unstable and tend to aggregate in the alcoholic solutions typically used for wet methods [4]. Therefore, it is attractive to make Ag nanoparticles coated with a layer of SiO_2, by flame spray pyrolysis (FSP), a dry, faster, more versatile and with a proven scalability process [7, 8].

Recently, Teleki *et al.* [9] reported the in-situ coating of TiO_2 nanoparticles with an ultrathin SiO_2 layer, using a modified FSP unit, in which the SiO_2 precursor was injected above the FSP burner after the formation of core TiO_2 particles had been completed. However, unlike metal oxide nanoparticles which can be easily coated with SiO_2, Ag nanoparticles are considered not to be suitable for direct coating due to their low chemical affinity to SiO_2 [3, 4].

Here, Ag nanoparticles dispersed within an amorphous SiO_2 matrix or coated with a nanothin layer of SiO_2 are made by FSP, of solutions of silver nitrate in ethanol and diethylene glycolmonobutyl followed by in-situ SiO_2 coating from hexamethylsiloxane (HMDSO) vapor injected downstream of the FSP burner. For the SiO_2 coated nanoparticles, the size of the Ag core particles was controlled by varying the distance above the FSP burner. The as produced particles were characterized by TEM, X-ray diffraction (XRD), nitrogen adsorption (BET) and UV/vis spectroscopy.

2 EXPERIMENTAL

Silver nitrate (Fluka, purity >99%) and hexamethyldisiloxane (HMDSO, Aldrich, purity >97%) were used as silver and silicon precursors, respectively. Appropriate amount of the silver nitrate was dissolved in ethanol (Alcosuisse) and diethylene glycolmonobutyl ether (Fluka, purity >98%) with a volume ratio 1:1 and stirred at room temperature for 3 hours. Immediately before the precursor solution was fed into the FSP setup, appropriate amount of HMDSO was added and stirred for a few minutes. The total (Ag and Si) metal concentration was 0.5 M. The Ag content was 70 and 85 wt % (*70Ag/SiO₂* and *85Ag/SiO₂*). The particle synthesis was carried out using a flame spray pyrolysis (FSP) reactor which is described in detail elsewhere [7]. The synthesis of the SiO_2-coated particles was carried out using a modified enclosed FSP reactor [9]. In brief, the FSP reactor was enclosed with a metallic tube (internal diameter, ID = 40 mm) on top of

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which a metallic ring with 12 equidistant openings was placed, at two (15 and 25 cm) burner-ring-distances (BRDs). The SiO_2 coating was applied after the core particles formation had been completed, by the injection of vapor HMDSO from the metallic ring. Through these openings, nitrogen gas (purity >99 %), carrying HMDSO vapor, the precursor source for the SiO_2 coating, was injected along with 15 L/min nitrogen (N_2 mixing) at room temperature. The HMDSO vapor was supplied by bubbling 0.8 L/min nitrogen through approximately 350 mL liquid HMDSO in an 500 mL glass flask which was kept at 10 °C with cooling water, adding approximately 5.7 g/h of SiO_2, at saturated conditions, in the product [10]. The total Ag content of the coated particles was kept constant at 70 wt %.

The produced particles were characterized by TEM (FEI; LaB6 cathode, operated at 300 kV, point resolution ~2 Å) and EDAX analysis (EDXS; detector attached to the Tecnai F30 microscope), X-ray diffraction (Bruker AXS D8 Advance spectrometer (Cu Kα, 40 kV, 40 mA), specific surface area (*SSA*) of the samples was measured by five-point nitrogen adsorption at 77 K (BET: Micrometrics Tristar 3000) after degassing the samples at 150 °C for 1.5 hours in nitrogen. The optical properties were examined by UV/vis spectroscopy (Cary Varian 500), by dispersing in deionized water 50 μg/ml of the as-prepared nanoparticles.

3   RESULTS & DISCUSSION

Ag nanoparticles dispersed within an amorphous SiO_2 matrix (uncoated), or coated by a thin SiO_2 layer were synthesized by FSP. The uncoated particles were produced by an open FSP setup unit, while the SiO_2 coated by a modified enclosed unit. Figure 1 shows the XRD patterns of the as-prepared nanoparticles. The spectra have been normalized for the (111) peak. Starting from the bottom, the patterns of the uncoated particles are presented (*70Ag/SiO_2* and *85Ag/SiO_2*), followed by the patterns of the SiO_2 coated ones, for two different BRDs (*70Ag/SiO_2-15cm* and *70Ag/SiO_2-25 cm*). The peak positions on top indicated by the black lines in this figure correspond to the (111), (200) and (220) crystal planes of the Ag metal (ICSD nr. 064995). It is observable that the obtained peaks correspond to this metallic structure, for all the products. Additionally, the particle sizes, calculated by using the Rietveld method for the (111) peak, are also shown.

In flame synthesis, the particle size depends on several parameters, such as the flame temperature, the particle residence time and the concentration of the precursor which is used [7]. In respect to the precursor concentration which is used, larger sizes are obtained for higher concentrations. However, for the uncoated particles, in respect to the d_{XRD}, it can be observed that the Ag average particle sizes are equal for the two different Ag contents, indicating that the presence of SiO_2 inhibits the further growth of the Ag nanoparticles. On the other hand, when the d_{XRD} sizes of the coated samples are examined, it can be observed that for a higher BRD, larger particle size is obtained. This could be attributed to the larger residence time that the Ag nanoparticles have for the higher BRD, before their entrapment by the SiO_2, and due to the fact that an open flame has much higher cooling rates than an enclosed one. Therefore, it can be concluded that by using the modified enclosed setup, the size of the Ag nanoparticles can be precisely controlled, while when the open FSP setup is used, the size of the Ag nanoparticles is influenced mostly by the SiO_2.
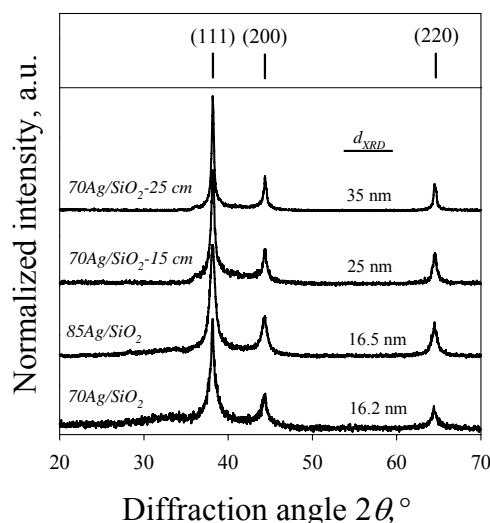

Figure 1: Normalized spectra of the as-prepared nanoparticles. The black lines on top represent the peak positions of the Ag metal structure. The d_{XRD} calculated by the Rietveld method is also shown.

The values of the specific surface area (*SSA*) of the produced samples can be observed in Table 1. It is noticeable that the uncoated samples have higher values, while the coated, lower ones. In case the enclosed setup is used, the particles have larger residence time in higher temperatures than when the open setup is used and thus, the particles grow bigger, resulting in lower *SSA*. When the two coated samples are compared, the one with the higher BRD has lower *SSA*, which is line with the Ag core particle sizes which are observed from the XRD analysis, having the higher *SSA* values for the smaller particle sizes.

Table 1: The values of the *SSA* for the as-produced nanoparticles.

Sample	SSA, m^2/g
70Ag/SiO_2	107
85Ag/SiO_2	70
70Ag/SiO_2 – 15 cm	53
70Ag/SiO_2 – 25 cm	35

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The morphology of the produced particles can also be observed from the obtained TEM images. In Figure 2, two TEM images of the uncoated particles *70Ag/SiO₂* (a) and the SiO₂ coated *70Ag/SiO₂-15cm* (b) are shown. It can be observed that the uncoated Ag particles are dispersed within an amorphous SiO₂ matrix, while the coated ones have a SiO₂ layer surrounding them.
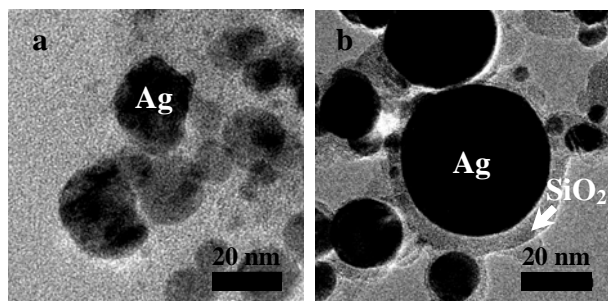

Figure 2: Two TEM images of the uncoated particles *70Ag/SiO₂* (a) and the SiO₂ coated *70Ag/SiO₂-15cm* (b) are shown.

The optical properties of the produced nanoparticles are presented in Figure 3. The UV/vis spectra of the produced nanoparticles are shown. The spectra have been normalized in respect to the strong absorption band at ~400 nm, which corresponds to the plasmon resonance frequency. For the uncoated *70Ag/SiO₂*, there is the plasmon resonance frequency peak at ~400 nm present [11]. However, as the Ag particle size is increased, in the spectrum corresponding to the *85Ag/SiO₂*, apart from the sharp peak at ~400 nm, there is also a broad hump appearing at ~520 nm, due to the increased state of aggregation and the larger particle size, as predicted by the literature [11]. For the SiO₂ coated samples, it also observable that for the lower BRD, there is only the peak at ~400 nm, however, as the Ag core particle size is increased, there is a second peak appearing at higher wavelengths. For the higher BRD, the peak at higher wavelengths is more intense, in respect to the 400 nm peak, than the one resulting from the open flame *85Ag/SiO₂*. It is observable that even though the d_{XRD} sizes of the two samples resulting from the open flame are similar, there are differences in the corresponding UV/vis spectra. Therefore, it seems that the band at higher wavelengths is not only dependent on the primary particle size of the Ag nanoparticles, but also other factors affect it, such as the aggregation state and the size of the aggregate structures, as reported by the literature [11].

Therefore, with both FSP setups, it is possible to control the optical properties of the produced Ag nanoparticles, by controlling the Ag particle sizes. The advantage of the coated particles lies in the possibility of fine tailoring the Ag nanoparticles sizes, and thus, tuning their optical properties depending on the desired application. Moreover, the SiO₂ layer surrounding the Ag core particles is easier to be functionalized and thus, organic molecules can be conjugated on its surface, a property extremely important in applications such as bio-labeling [6].
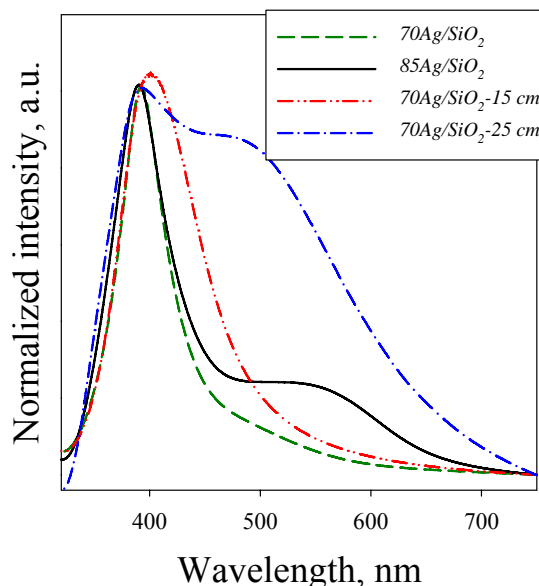

Figure 3: Normalized UV/vis spectra of the as-prepared samples.

4 CONCLUSIONS

Silver nanoparticles dispersed within an amorphous SiO₂ matrix or coated by a SiO₂ layer were produced by FSP. The uncoated Ag/SiO₂ nanoparticles were produced by an open FSP setup, while the synthesis of the SiO₂ coated by using a modified enclosed setup. In case the open setup was used, the Ag particle sizes depend mostly on the Ag content, however, limitation in the controllability due to the SiO₂ do exist. However, when the enclosed setup is used, precise control over the Ag core particle size can be achieved. Depending on the BRD, larger Ag particles are obtained for higher BRDs. All the produced Ag nanoparticles exhibited a peak at ~400 nm in their UV/vis spectra, characteristic peak corresponding to the plasmon resonance frequency of Ag nanoparticles. The precise Ag core size controllability, as well as the SiO₂ coating layer, are properties extremely important in several applications, such as bio-labeling.

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