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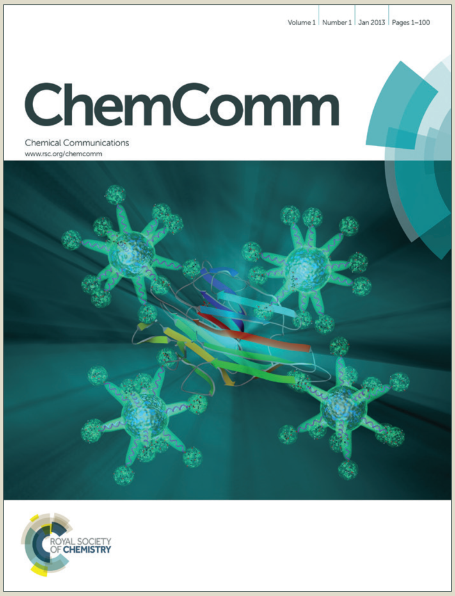

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ARTICLE

Effect of Surface Carbon Coating on Sintering of Silver Nanoparticles: In-situ TEM Observations

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In this work, *in-situ* transmission electron microscopy heating has been used to investigate the effects of a carbon capping layer on sintering of silver nanoparticles. For the first time, we make direct and real-time measurements of surface diffusivity of silver in nanoparticles coated with carbon. We observe that the carbon surface coatings may significantly inhibit sintering in silver nanoparticles.

Nanoparticles exhibit unique size-dependent properties due to the large fraction of their surface atoms compared to bulk materials [1-5]. These unique physical, chemical, optical and electronic properties are already being exploited for applications in areas such as chemical catalysis, microelectronics, biological sensors and other applications [6-12]. However, in many of these applications it is important that nanoparticles remain thermally stable. Due to their large surface area-to-volume ratio, nanoparticles have a strong tendency to coalesce and sinter during processing or usage, over short time scales, which can lead to significant changes in their desirable properties with subsequent changes in behavior and performance.

One important question is whether the coalescence and sintering of nanoparticles is affected by the presence of any type of surface coating. T. Vystavel *et al.* [13] have shown that an oxide shell inhibits coalescence of metal nanoparticles and that the contact between the nanoparticles and the substrate appears to be significantly more dynamic that previously thought. Y. Chen *et al.* [14] reported that the presence of ligands between nanoparticles of gold dramatically change the sintering process. Magdassi et al. [15], showed that sintering of silver is inhibited by an organic layer on the surface. However, the influence of surface films on the effective surface diffusivity has not been directly measured. In this context, carbon coatings are particularly relevant because 1) nanoparticles are often deposited on a carbon substrate, 2) hydrocarbon species are usually intentionally added during many synthesis processes to produce and stabilize the size of nanoparticles. These hydrocarbons pyrolyze during sintering, resulting in carbon residue as well as gas evolution and 3) carbon may be adsorbed on the surface of nanoparticles due to atmospheric exposure.

To address this issue, the primary objective of this paper is to determine how the presence of a carbon layer on silver nanoparticles will influence sintering, in particular neck growth and surface diffusivity. Although it is true that the presence of carbon on particles surfaces in the TEM is inevitable, we have compared two systems - one where carbon was intentionally added so the amount of carbon is significant and easily visible on the surfaces of nanoparticles and another where initially there is no carbon. In the former, the carbon is semi-amorphous, showing some indication of graphitization, which is typical of what is observed after pyrolysis of organics. Since most nanoparticles are processed with organics, the system that was studied is a good model system for the most common methods for producing nanoparticles. We have also compared different regions of the particles that contain carbon where the carbon content varies from region-to-region.

To accomplish this goal, *in-situ* transmission electron microscopy (TEM) heating experiments were carried out, which allowed us to observe the sintering process in real-time.

Two different sets of samples were used in this work. Silver nanoparticles with nominal sizes of 15 nm and 40 nm were obtained from Nanotechnologies Inc. The nanoparticles were synthesized by a pulsed plasma dry synthesis method and a carbon additive was added during the manufacturing process to prevent agglomeration of the nanoparticles by physically separating them. In addition, silver nanoparticles produced by a novel laser ablation of microparticle aerosol (LAMA) technique [16] were also used. In either case, the particles were not covered with any organic molecules.

For TEM observation, the as-received nanoparticles from Nanotechnologies Inc. were first dispersed in ethanol and placed in an ultrasonic bath for ten minutes to reduce particle agglomeration. The nanoparticles in solution were then deposited onto an Aduro^{TM} heater chip which was later placed in a Protochips heating holder for *in-situ* TEM experiments. In the case of the LAMA-produced nanoparticles, samples were prepared by depositing them directly onto a bare silver wire in order to minimize the presence of carbon on the sample.

In both cases, the nanoparticles were heated *in-situ* using a novel Aduro^{TM} heating stage [17] (Protochips Inc., Raleigh, NC).

The heating stage uses a disposable micro-electro-mechanical system (MEMS) device that serves both as the heating element and the specimen support grid and the holder have electrical feed-throughs that connect to an external power supply. The MEMS device is a 150 nm thick, 500 µm × 500 µm, free standing membrane made from a conductive ceramic material that is suspended on a 4 mm × 6 mm silicon chip. For electron transparency, the ceramic membrane is patterned with a series of 6 µm diameter holes, which are subsequently overlaid with a holey carbon film, which support the nanoparticles. Joule heating occurs when electrical current is forced through the ceramic membrane and the current is used to control the temperature. The current versus temperature response of the heating device was calibrated at the factory using an imaging pyrometer in a vacuum probe station (at a pressure similar to what is used in a TEM column). This heating stage enables very fast heating rates (10^6 °C/s) with an extremely low thermal drift even at high temperatures due to its low thermal mass, unlike conventional heating holders. This allows for isothermal experiments to be carried out in the TEM as desired temperatures can be achieved nearly instantaneously. The as-received heater chips were further checked for accuracy in our laboratory using a known solid-to-vapor phase transformation to determine their accuracy for temperature measurements [18]. As discussed in [18], the beam can increase the temperature by 50-100 ˚C. However, such a small temperature increase is not sufficient to explain the large decrease in surface diffusivity that we observe in this paper.

To assess the effect of a carbon surface coating on sintering of silver nanoparticles, *in-situ* heating experiments were conducted on nanoparticles where a carbon coating was present on the surface. In general, of course, smaller nanoparticles may participate in the coalescence process of larger nanoparticles. However, in our experiments, we were careful in selecting nanoparticles, which were not affected by surrounding smaller particles. Figure 1 shows sintering of two nanoparticles at 300 °C, where more carbon residue can be observed on the top of the nanoparticles (indicated with a red arrow in the second frame), compared to the bottom. Under these conditions, as shown by the sequence of images in Figure 1, the neck grows more readily at the bottom region of the nanoparticles than at the top, which is due to the carbon coating acting as a steric barrier to sintering. Many of the larger particles observed, such as those depicted in Figure 1, contained twins before heating. However, the twins were rather stable, as they are twin loops running along the diameter of the particle. In addition, during many events, we observed the coalescence of particles without a significant change of the twin structure.

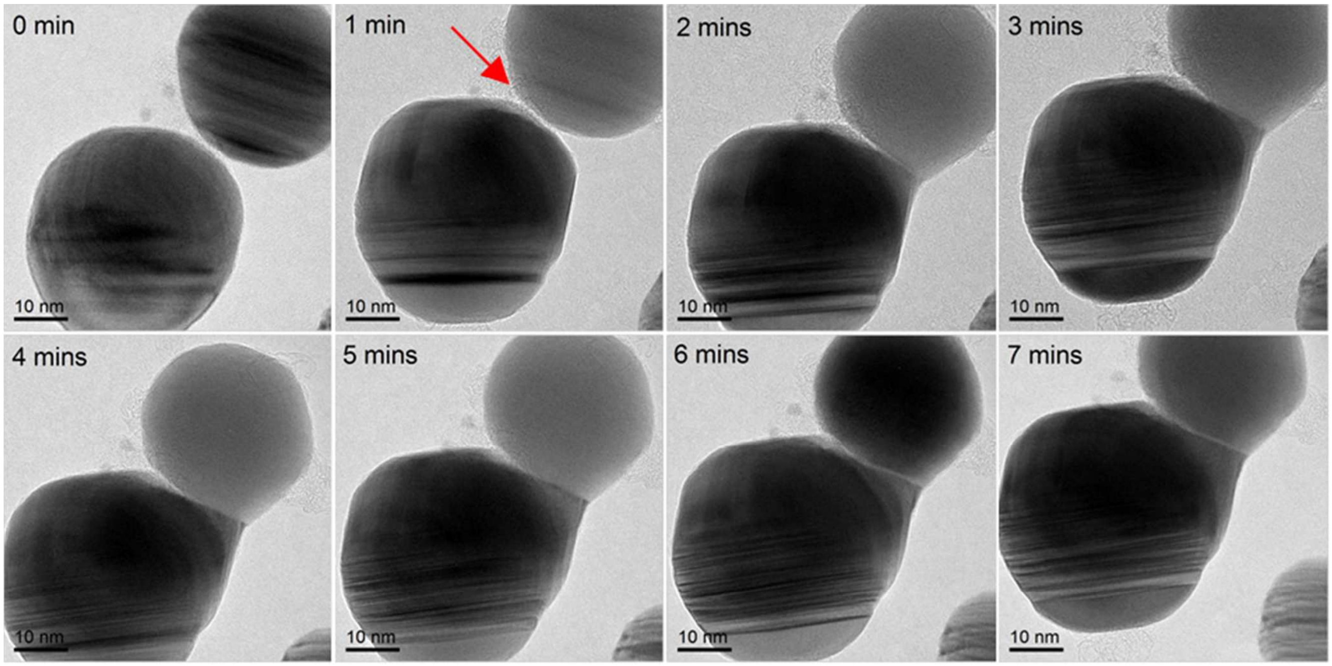

Figure 1: A sequence of *in-situ* TEM heating images during sintering of two silver nanoparticles at 300 °C showing that the carbon residue on the surface of nanoparticles can prevent neck growth.

Figure 2 shows another example of two 15 nm silver nanoparticles coated with carbon and sintered at 300 °C. In this case, the carbon appears to cover the neck region and therefore prevents further neck growth after about 20 minutes. The neck region then starts to shrink, while the nanoparticle on the left grows larger at the expense of the smaller nanoparticle after approximately 18 minutes, possibly by mass transfer through the constrained neck region. As shown in Figures 1 and 2, the carbon that typically resides on the surface of nanoparticles, either because it was intentionally added or because it is a remnant of the process used to produce and stabilize the nanoparticulate colloid during processing, serves as a barrier to sintering of nanoparticles. To better understand this process, we followed a procedure described previously by Asoro *et al.* [19] to calculate the surface diffusion coefficient, D_s of silver nanoparticles in the presence of a carbon coating. For the case of silver nanoparticles ranging in size from 12 nm - 40 nm in diameter, we found D_s to be in the range 4.2×10^{-16} cm^2/s - 1.1×10^{-20} cm^2/s at temperatures of 200 °C - 400 °C, which is several orders of magnitude lower than the values obtained from bulk silver at high temperatures and extrapolated to room temperature (10^{-13} cm^2/s). Thus, these measured values of surface diffusivity, due to the presence of carbon or adsorbed species on the surface of our nanoparticles, do not represent the intrinsic surface diffusivities of silver but an effective diffusivity of silver nanoparticles under realistic conditions.

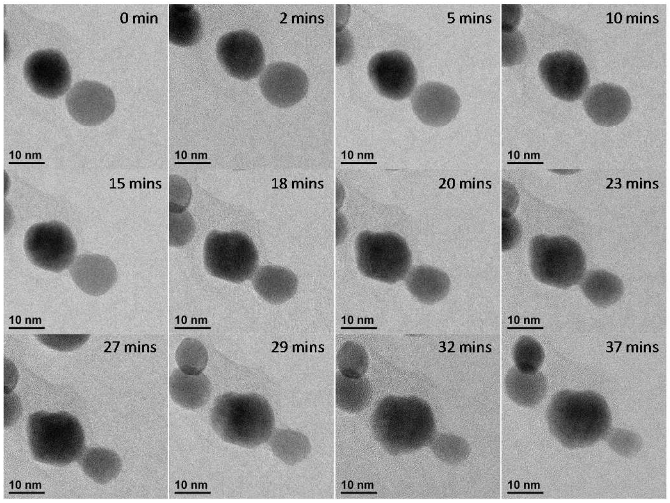

Figure 2: *In-situ* TEM heating images of two 15 nm silver nanoparticles at 300 °C shows that carbon coatings on the surface of nanoparticles can slow down neck growth.

These results are consistent with diffusion coefficients for bulk silver that was previously reported for pyrolytically deposited carbon and measured from helium scattering experiments [20]. To further investigate the effect of carbon, sintering experiments were conducted on LAMA silver nanoparticles deposited directly on a thin silver wire, which was then placed on a customized Protochips grid that did not contain holey carbon. Figure 3 is a sequence of *in-situ* TEM images showing sintering of a 40 nm LAMA silver nanoparticle with a 35 µm silver wire at 400 °C.

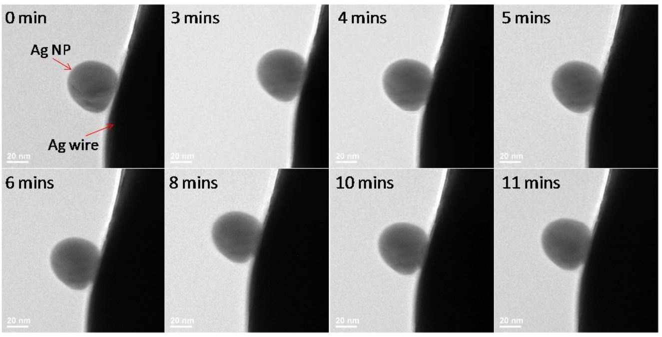

Figure 3: *In-situ* TEM images showing sintering of a 40 nm LAMA silver nanoparticle with a 35 µm diameter silver wire at 400 °C.

We note that the silver nanoparticle formed a neck with the silver wire by the time the first image could be captured, after approximately 3 minutes. Subsequent observations did not reveal significant additional neck growth during heating for 11 minutes. Although the amount of surface contamination on the wire and nanoparticle surface was reduced compared to previous experiments on carbon support, there is still some contamination that is visible. This contamination could have occurred during atmospheric exposure when transferring the wire to the grid. Raman spectra of LAMA-produced silver nanoparticles also show some extra peaks due to some C-H species present in the sample after exposure to atmospheric conditions, suggesting that the nanoparticles can easily absorb some gases or hydrocarbons when exposed to the atmosphere.

For the LAMA-type nanoparticles, the sphere-on-plate sintering geometry derived by Kuczynski [21] was used to calculate the surface diffusivity from our measured values of particle radius and neck radius with time. For a 40 nm nanoparticle at 400 °C, the surface diffusivity was determined to be $1.2 \times 10^{-14} - 1.8 \times 10^{-14}$ cm^2/s, which is two orders of magnitude greater than the value obtained previously for the same size particles with carbon surface coating and at the same temperature. It should be noted that this calculation only gives a lower bound of the surface diffusivity value since the neck growth is first measured after 3 minutes, and it is possible that sintering occurred earlier but could not be captured fast enough. However, these results provide an insight into the effects of the carbon surface coating on the kinetics of sintering in nanoparticles. From these experiments, we suggest that when the surface of the silver nanoparticle is covered with carbon, as shown schematically in Figure 4, the diffusion of atoms from the surface to the neck occurs through the carbon.

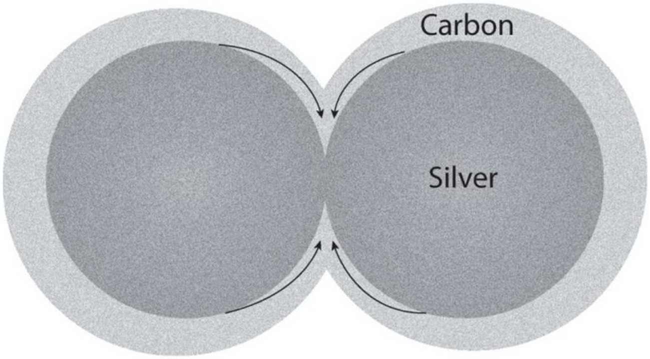

Figure 4: Sintering of two nanoparticles covered with a carbon surface coating, showing that for the neck to grow, atomic diffusion from the surface to the neck occurs through the carbon.

As the neck grows, the carbon surface coating is pushed outwards from the neck region to drive further growth, but this process is slower than the surface diffusion of pure silver, which results in a decrease in the observed diffusivity values in the presence of carbon.

In-situ TEM heating was used to make direct, real-time measurements of nanoparticle size, and neck growth during sintering, which allowed us to calculate surface diffusivity values for silver nanoparticles in the presence of a carbon coating. Our calculated values of D_s (4.2×10^{-16} cm^2/s - 1.1×10^{-20} cm^2/s) for these silver nanoparticles are significantly lower than previously reported values for bulk silver measured at high temperatures and extrapolated to lower temperatures. This confirms that the presence of carbon on the surface of nanoparticles can significantly inhibit sintering in nanoparticles. For example, sintering experiments performed between a nominally bare silver nanoparticle and a silver wire showed at least a two orders of magnitude increase in surface diffusivity compared to carbon-capped nanoparticles.

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Notes and references

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1. M. A. El-Sayed, *Accounts of Chemical Research*, 2001, **34**, 257.
2. W. Eberhardt, Surface Science, 2002, **500**, 242.
3. Alan S. Edelstein and R. C. Cammarata, *Nanomaterials: synthesis, properties, and applications*, 1998, Institute of Physics Publishing, Bristol, U.K.
4. P. Buffat and J. P. Borel, *Physical Review A*, 1976, **13**, 2287.
5. P. R. Couchman and W. A. Jesser, *Nature*, 1977, **269**, 481.
6. Z. Tang and N. A. Kotov, *Advanced Materials*, 2005, **17**, 951.
7. R. Shenhar, T. B. Norsten, and V. M. Rotello, *Advanced Materials*, 2005, **17**, 657.
8. C. J. Murphy, T. K. Sau, A. M. Gole, C. J. Orendorff, J. Gao, L. Gou, S. E. Hunyadi, and T. Li, *The Journal of Physical Chemistry B*, 2005, **109**, 13857.
9. H. K. Seung, P. Heng, P. G. Costas, K. L. Christine, M. J. F. Jean, and P. Dimos, *Nanotechnology*, 2007, **18**, 345202.
10. V. Subramanian, J. M. J. Frechet, P. C. Chang, D. C. Huang, J. B. Lee, S. E. Molesa, A. R. Murphy, D. R. Redinger, and S. K. Volkman, *Proceedings of the IEEE*, 2005, **93**, 1330.
11. B. Crone, A. Dodabalapur, A. Gelperin, L. Torsi, H. E. Katz, A. J. Lovinger, and Z. Bao, *Applied Physics Letters*, 2001, **78**, 2229.
12. S. P. Price, J. Henzie, and T. W. Odom, *Small*, 2007, **3**, 372.
13. T. Vystavel, S.A. Koch, G. Palasantzas and J.T.M. De Hosson, *Journal of Materials Research*, 2005, **20**, 1785.
14. Y. Chen, R. E. Palmer, and J. P. Wilcoxon, *Langmuir*, 2006, **22**, 2851.
15. S. Magdassi, M. Grouchko, O. Berezin and A. Kamyshny, *ACS Nano*, 2010, **4**, 1943.
16. W. T. Nichols, J. W. Keto, D. E. Henneke, J. R. Brock, G. Malyavanatham, M. F. Becker, and H. D. Glicksman, *Applied Physics Letters*, 2001, **78**, 1128.
17. L. F. Allard, W. C. Bigelow, M. Jose-Yacaman, D. P. Nackashi, J. Damiano, and S. E. Mick, *Microscopy Research and Technique*, 2009, **72**, 208.
18. M. A. Asoro, D. Kovar and P. J. Ferreira, *ACS Nano*, 2013, **7**, 7844.
19. M.A. Asoro, D. Kovar, Y. Shao-Horn, L.F. Allard, P. J. Ferreira, *Nanotechnology*, 2010, **21**, 025701.
20. P. Offermann, *Journal of Nuclear Materials*, 1977, **64**, 249.
21. G. C. Kuczynski, *Trans. AIME*, 1949, **185**, 169.