Catalytic nanoparticles for carbon nanotube growth synthesized by through thin film femtosecond laser ablation

C. M. Rouleau,[1*] M. Tian,[2] A. A. Puretzky,[1] M. Mahjouri-Samani,[1] G. Duscher,[2] and D. B. Geohegan[1]

[1]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 37831-6488

[2]Department of Materials Science and Engineering, University of Tennessee at Knoxville, Knoxville, Tennessee, 37996-2100

ABSTRACT

The synthesis of metal nanoparticles by femtosecond laser vaporization of nm-thickness metal films is explored with the goal of comparing the salient features of femtosecond-based through thin film laser ablation (TTFA) to that of ns TTFA, and testing the feasibility of direct synthesis of clean nanoparticle alloys to explore the synthesis of carbon nanotubes by chemical vapor deposition. It is demonstrated that evaporated metal films are cleanly removed from quartz substrates using the technique, producing a highly forward-directed plume of nanoparticles (angle of divergence of ~2.5º) which were cleanly deposited onto different supports for analysis. TEM showed the nanoparticles were spherical with diameters that ranged from a few nm to hundreds of nm in a bimodal fashion. Unlike ns-TTFA, it was found that raising the pressure had no effect on the intensity of the smaller mode within the distribution, suggesting that nanoparticle formation by gas phase condensation was not at play under the present conditions. Close examination of size distributions from a 20 and 10nm Pt film revealed an 80nm downshift in the position of the large mode within the distribution, suggesting film thickness may provide a route to controlling the modal distribution of nanoparticles produced by this method. Lastly, particles sourced by a Fe/Mo bilayer film were found to be effective in growing single wall carbon nanotubes by atmospheric chemical vapor deposition, indicating sufficiently small and catalytically active particles were produced.

Keywords: femtosecond laser vaporization, through thin film laser ablation, nanoparticle synthesis, nanotube growth

1. INTRODUCTION

Metal nanoparticles promise a number of applications in the fields of catalysis, optoelectronics, and medicine,[1] and when compared to chemical synthesis methods, laser-based techniques offer a clean, surfactant-free approach for producing a large variety of compositions with a range of sizes.[2, 3] Laser-induced forward transfer (LIFT) is particularly useful as it affords control over nanoparticle placement for patterning as well as single particle applications.[4-10] In LIFT, pulse durations ranging from ns to fs have been employed, and with few exceptions, the technique is normally performed under ambient conditions with the source and receiving substrate in near-contact. However, Murray et al.[11]and Tseng et al.[9] have recently relaxed these norms, and have used self-described through thin film ablation (TTFA) and laser-induced jets of nanoparticle arrays, respectively, to create nanoparticle deposits using ns laser sources. It is worth noting that the duration of a ns-laser pulse is orders of magnitude greater than the few ps required for thermal or mechanical equilibration in a typical target film, and consequently, it can be argued that the nanoparticles produced by these latter techniques were largely the result of condensation of a laser-induced plume in a background gas. Femtosecond pulses, on the hand, represent the opposite extreme, easily promoting thermal and/or mechanical confinement, but nanoparticle distributions produced using this laser source under conditions similar to Murray et al.[11] are not well-understood.

In principle, as shown in Figure 1, this understanding may offer the opportunity to produce a wide variety of metal nanoparticles to explore catalytic activity on different catalyst supports, for example, and by using gradient thin films as targets, a wide range of stoichiometries may be produced rapidly and cleanly in a combinatorial fashion.

*rouleaucm@ornl.gov; phone 1-865-574-5499

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Here, we implement a TTFA system using a femtosecond laser source, and use it to study the divergence, morphology, and size distributions of Pt metal nanoparticle deposits, and test the feasibility of synthesizing clean nanoparticle alloys of Fe/Mo to explore the synthesis of carbon nanotubes by chemical vapor deposition.

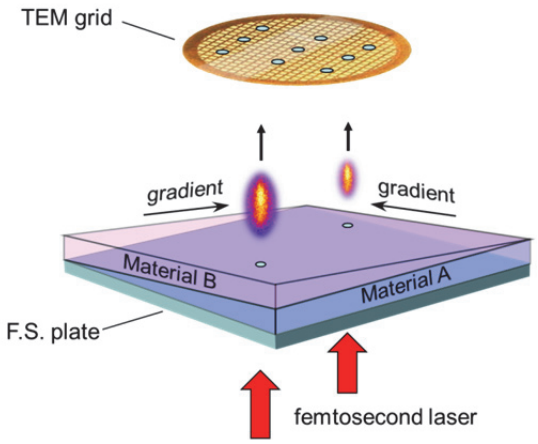

Figure 1. Concept of using femtosecond through thin film laser ablation to explore alloy nanoparticles. Two materials (A and B) are deposited in orthogonal gradients on a fused silica plate, and through-thin film laser vaporization at different locations locally removes different ratios of compositions A:B to produce nanoparticles in highly forward-directed plumes which can be deposited onto TEM grids for analysis, as shown, or onto other acceptor substrate.

2. METHODOLOGY

Through thin film ablation (TTFA) by femtosecond laser irradiation was implemented as shown in Figure 2. Here, nm-scale films were deposited by e-beam evaporation onto fused silica source substrates, and placed within millimeter proximity to an acceptor substrate inside a small, windowed vacuum chamber. The chamber was actively pumped to ~10^{-5} Torr or filled with a background gas during material processing, and it was attached to a motion controlled XYZ stage so that many equivalent locations on the source substrate could be visited in the course of an experiment. As shown in the figure, the femtosecond laser (800nm, 40fs) was delivered to the sample using a projection beamline that was comprised of a set of crossed slits, a 1 meter focal length field lens, and a 10X infinity corrected long working distance objective lens having a focal length of ~20mm. Note that this combination of lenses resulted in a magnification of ~0.02X. To control laser fluence during material processing, two motion-controlled, continuously variable neutral density (ND) filters were placed in opposite directions and moved relative to each other. In contrast to moving a single continuously variable ND filter in the path of the beam, this arrangement provided attenuation that was spatially uniform. To further attenuate the beam and promote uniform illumination of the crossed slits, and a 3X beam expander was also used. Note that with the slits and source substrate placed at the object and image planes of the beamline, respectively, a rectangular 20x25μm^2 spot with nearly uniform intensity was achieved at the film/substrate interface. Also note that uniform removal of a 20nm Pt film, for example, was achieved for fluences in the range of 40-60mJ/cm^2. Lastly, laser beam targeting and focus adjustment was achieved using a fiber illuminator, dichroic beam splitter, megapixel CCD camera, pellicle beam splitter, and associated tube lenses. As shown within the CCD image in the figure, this arrangement achieved a horizontal field of view of ~225um, easily allowing observation of the film/substrate interface, illumination of the slit with the seed laser, and subsequent quality of the ablated spot.

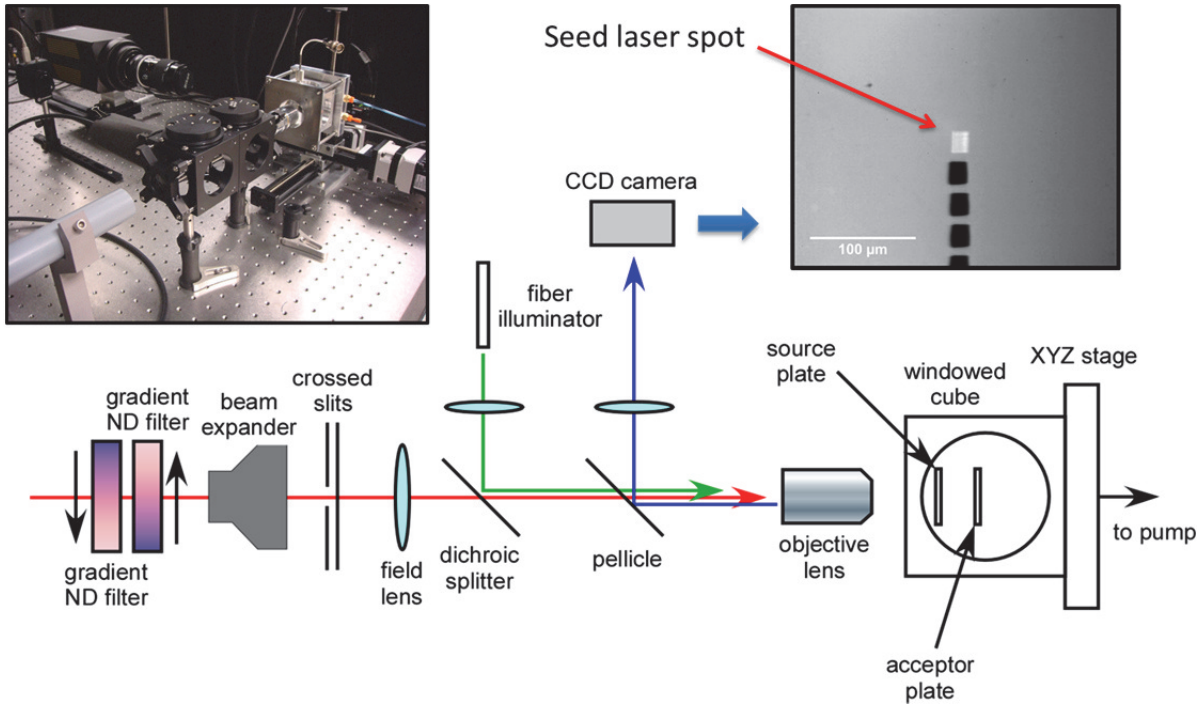

Figure 2. Experimental setup for through thin film laser ablation using femtosecond laser irradiation. Crossed slits, field lens, and objective comprise a projection beamline with a magnification of 0.02X. Spatially uniform beam attenuation was accomplished using two continuously variable ND filters placed in opposing directions. Uniform illumination of the slits was achieved using a 3X beam expander, and live imaging for targeting, focusing, and diagnostics was realized with a fiber illuminator, dichroic splitter, megapixel CCD camera, pellicle splitter, and associated tubes lenses. When combined, the horizontal field of view of the system was ~225µm. The processing chamber was ~250cm^3, was actively pumped to 10^{-5} Torr for experiments require vacuum, and resided on a XYZ stage so that numerous unique locations on the source substrate could be visited.

3. RESULTS

3.1 Directionality, morphology, and size distribution of ejecta

In experiments involving ablation of a 20nm Pt film in vacuum and collection of the material on a small 5x5mm^2 Si chip, we found that the ejecta was highly forward directed. Here, the Si chip was placed 5mm from the source substrate, and kept stationary with respect to the beamline. The source substrate, on the other hand, was rastered in front of the chip so that fresh material was available for every laser shot. Nearly 4000 shots of material were directed at a single location on the Si receiver so as to produce maximum contrast when examined with an optical microscope, and as shown in Figure 3a, a 'spot' of material was produce that had a FWHM of ~250µm. This, combined with a source dimension of ~20µm and a propagation distance of 5mm, resulted in an angular divergence of ~2.5º, which is considerably more narrow than 'plumes' of material found in conventional ablation of bulk materials.

Other experiments in vacuum involved collection of the same material on a lacey carbon grid that was placed on the acceptor substrate, and we found that the deposit was composed of nanoparticles whose size distribution was bimodal. Note that in contrast to experiments involving deposition of material at a single location, these experiments involved moving the source and acceptor substrates as a unit in front of the laser beam so that material was 'spread' over a 2x2mm^2 area on the grid surface. This arrangement avoided particle pileup as in the former case, and made particle statistics by examination of TEM micrographs more tractable. As shown in Figure 3b and c, the nanoparticles were spherical, and ranged in size from a few nm to hundreds of nm. Most interesting, however, was the observation that the distribution was bimodal with one mode centered near 10nm and the other near 200nm. This result is currently not well-

understood, and MD simulations are planned to gain insight into this result, but what is known so far is that the smaller mode was not due to gas phase recombination of ablated atomic species (see section 3.2).

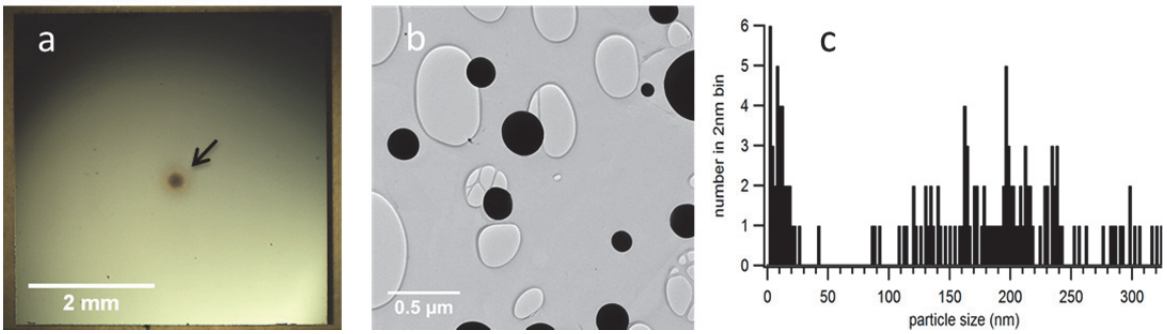

Figure 3. (a) Angular spread, (b) morphology, and size distribution (c) of nanoparticles synthesized by femtosecond through thin film ablation of a 20nm Pt film. Collection was performed in vacuum, 5mm from the source substrate, and with nearly 4000 unique laser shots. The FWHM of the 'spot' of material in (a) is ~250µm, and the FWHMs of the small and large modes in (c) are 10nm and 150nm, respectively.

3.2 Effect of pressure on nanoparticle size distribution

The question of whether the smaller mode in the bimodal distributions was due to gas phase recombination of ablated atomic species was answered by performing particle collection at 5mm in vacuum, and then again under 1 Torr Ar background gas, during TTFA of a 10nm Pt source film, and then comparing the particle statistics. As shown in Figure 4, both distributions were bimodal with one mode near 10nm and the other near 120nm, but in contrast to ns-ablation of thin metal films,[11] *no* change in the magnitude of the smaller mode was observed upon increasing the background pressure to 1 Torr. This observation supports the conclusion that gas phase condensation is not contributing to the particle size distributions under the present femtosecond laser-TTFA conditions. Lastly, it is interesting to note that as a result of using a 10nm source film in this experiment, an 80nm downshift in the position of the large mode was observed upon close comparison of the distribution in Figure 3c to that of the vacuum distribution in Figure 4. Although more work is required, this suggests that film thickness may be used to control the modal distribution of nanoparticles produced by this method.

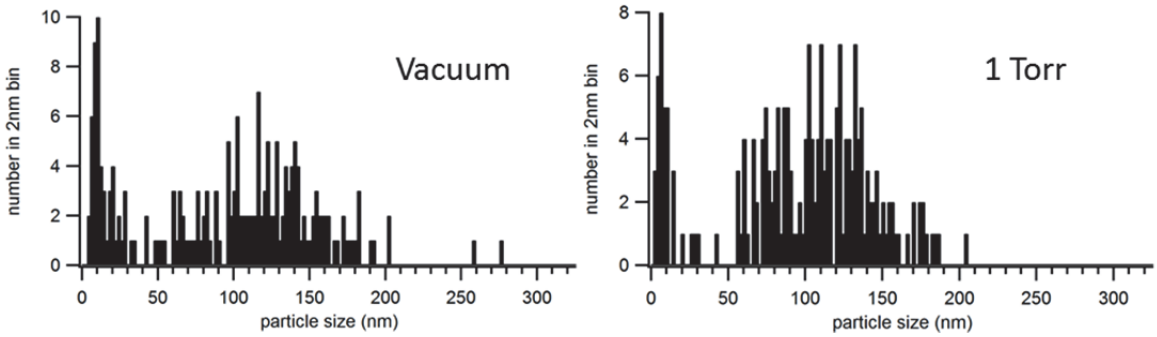

Figure 4. Comparison of resultant nanoparticle size distribution for a 10nm Pt film processed in vacuum and in a static fill of 1 Torr Argon gas. No significant change in the intensity of the smaller mode was observed, indicating it was not sourced by gas phase recombination of ablated atomic species as in TTFA using ns laser irradiation.[11] However, an 80nm downshift in the position of the large mode was noted upon comparison to Figure 3c, and suggests that film thickness may be used to control the modal distribution of nanoparticles produced by this method.

3.3 Carbon nanotube growth on Fe/Mo nanoparticles produced by fs-TTFA

To test the concept of alloy formation and determine if such particles would be sufficiently small and catalytically active for carbon nanotube growth, a Fe(1nm)/Mo(1nm) bilayer film was processed by fs-TTFA. Particle collection was

performed at ~5mm with a lacey carbon grid that was decorated with NanoDur® (spherical Al_2O_3 particles having an average diameter of 50 nm or less). Note that decoration of the lacey carbon grid was accomplished by sonicating ~100mg of NanoDur® in ~5 ml of MEOH for 1 minute, and then dabbing the mixture onto the grid with a swab. After collection in vacuum, the grid was then loaded into the chemical vapor deposition (CVD) reactor, and nanotube growth was performed for 1 minute at 1atm in a carrier gas of 2000sccm Ar + 200sccm H_2. Note that the growth temperature was 700°C and 10sccm of C_2H_2 was used as a source of carbon.

As shown in Figure 5a, resonant Raman spectroscopy confirmed the presence of single wall carbon nanotubes within several randomly selected grid holes, and using the relation d (nm) = 248 cm^{-1}/ω to estimate the diameters of the nanotube corresponding to each radial breathing mode, they ranged in diameter from 1.1 to 1.5nm. Although these findings were corroborated with TEM as shown in Figure 5b, we were not able to locate a nanotube and its source particle to determine the likely alloy responsible for growth. Instead, the nanotubes tended to be too long and obfuscated by the lacey carbon and NanoDur® particles to trace from beginning to end. Nevertheless, they confirmed that small-diameter nanoparticles suitable for SWNT growth exploration could be synthesized and isolated on appropriate catalyst supports by direct, femtosecond TTFA.

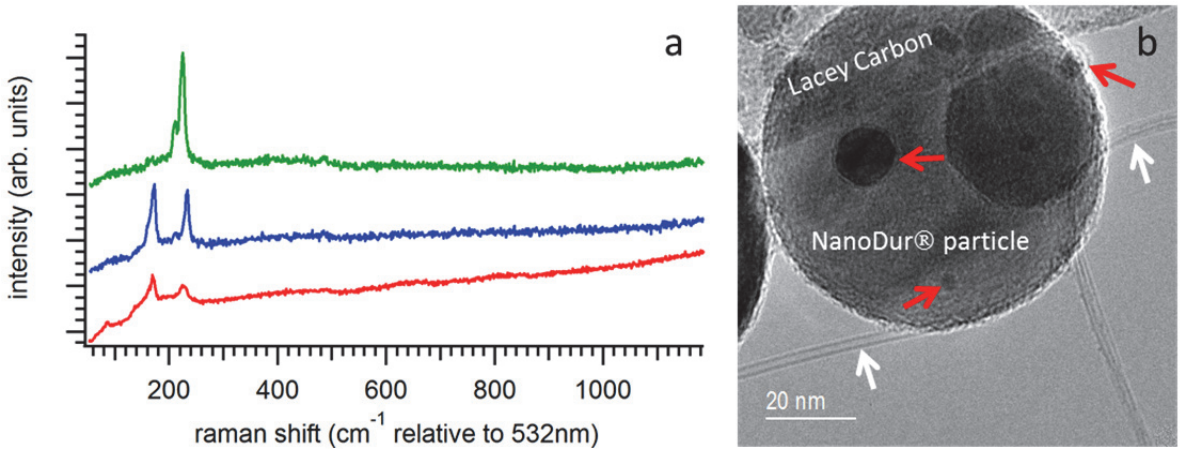

Figure 5. (a) Resonant Raman spectra (532nm laser excitation) taken from several locations on the lacey carbon grid after carbon nanotube CVD, and a representative TEM micrograph (b) showing single wall carbon nanotubes (white arrows), NanoDur® Al_2O_3 nanospherical catalyst support, metal nanoparticles (red arrows), and lacey carbon.

4. SUMMARY

In summary, we have developed a TTFA system that utilizes a femtosecond laser source, and have applied it to the generation of Pt nanoparticles as well as testing the idea of alloy nanoparticle formation. The plume of material was found to be highly forward directed with an angular spread of ~2.5º, making it well-suited for future application requiring localized placement of nanoparticle deposits. By collecting and analyzing the material on lacey carbon TEM grids, if was found that the Pt nanoparticles had a spherical morphology, with a particle sizes that ranged from a few nm to hundreds of nm. Interestingly, the particle size distribution was observed to be bimodal with one mode centered near 10nm and the other near 200nm. The widths of the small and large modes were 10nm and 150nm, respectively, but the overall result is currently not well-understood, and MD simulations are planned to elucidate why a bimodal distribution results under the present conditions. Generation of smaller particles by gas phase recombination of ablated atomic species was ruled unlikely under the present conditions, and particles sourced by a Fe/Mo bilayer film were found to be effective in growing single wall carbon nanotubes by atmospheric CVD, indicating sufficiently small and catalytically active particles were produced. Overall, these results perhaps point the way to a synthesis route for a number of tailored metastable nanoparticles, tens of nm in size, and capable of being delivered to a surface in a localized fashion.

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