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6879A-26, Session 6

Laser-induced alloying and size control of metal nanoparticles using femtosecond supercontinuum generation

S. Besner, S. Archambault, A. V. Kabashin, M. Meunier, Ecole Polytechnique de Montréal (Canada)

A femtosecond laser-based method has been developed for the size control of colloidal solution and metal alloys formation [1,2]. This method employs the self-transformation of the femtosecond laser irradiation into a broad white-light pulse which expands from ~365 to 1050nm and arises under high localization of the radiation in space and time. We demonstrate that the conversion efficiency of the initially 800-nm centered femtosecond radiation into a supercontinuum strongly depends on the pulse energy and focusing conditions and significantly enhances the energy transfer to the nanoparticles. In comparison to nanosecond laser fragmentation, this technique is able to form much smaller nanoparticles due to both the limited solution heating from direct laser absorption and to the limited thermal diffusion between the nanoparticles and the solution. The final size of the nanoparticles does not depend on the initial characteristics of the colloids, but strongly depends on the laser parameters and on the addition of chemical additives in the solution. Using this technique, we were able to finely tune the size of metallic particles (Au, Ag, Cu and Pt) between 2.5 and 30nm and make alloys by irradiation of their mixture. Such nanoparticles might be of good interest for Surface Enhanced Raman Scattering (SERS) and biosensing applications.

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2 S. Besner, A. V. Kabashin and M. Meunier, "Two-step femtosecond laser ablation-based method for the synthesis of stable and ultra-pure gold nanoparticles in water", *Appl. Phys. A-Mater*, 88, 269-72, 2007

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Bio-photosensitizer colloidal silicon nanoparticles produced by femtosecond laser ablation in liquid

D. Rioux, A. V. Kabashin, Ecole Polytechnique de Montréal (Canada); L. D. Lilge, S. Douplik, Univ. of Toronto (Canada); M. Meunier, Ecole Polytechnique de Montréal (Canada)

For their use in biological applications, nanoparticles have to be not only biocompatible but also ideally produced in only environmentally benign reducing agents and non-toxic materials for the stabilization of the nanoparticles. We propose to use a femtosecond laser-assisted method for the synthesis of small and low-dispersed silicon colloidal NP, all performed at room temperature in non-aggressive liquids such as deionized water and methanol or in nitrogen atmosphere, rendering this process very environment friendly. As we have shown previously for gold and other types of metallic nanoparticles, the use of femtosecond pulses presents the advantage over longer ones of producing very fine (few nanometers) and low dispersed NP, a necessity for most biomedical applications. Laser ablation of a silicon target in a liquid environment as well as in a low pressure nitrogen atmosphere was used to produce silicon nanoparticles. Structural analysis by transmission electron microscopy (TEM) showed ultrasmall amorphous nanoparticles (2.4 nm mean size) when ablation is performed in a liquid. Those particles are amorphous, resulting from the quenching of relatively hot liquid silicon in a disordered state due to rapid cooling of the particles in contact with the cold liquid. On the other hand, ablation in low pressure gas with subsequent dispersion of particles in liquid produces larger particles (10-30 nm) but with good crystalline structure since the cooling rate of these particles is much slower in gas than in the liquid. Over time, oxidation of nanoparticles in the liquid leads to enhancement of their photoluminescent properties. Such photoluminescent nanoparticles are of great interest as photosensitizers in photodynamic therapy (PDT) for treatment against tumor cells since they induce production of singlet

oxygen. Our nanoparticles already present signal of singlet oxygen generation and ongoing experiments are studying their effect on a panel of tumor cells in vitro.

6879A-19, Session 7

Ultrafast laser direct writing of resonant photonic devices

M. J. Withford, G. D. Marshall, M. Ams, N. Jovanovic, P. Dekker, A. Fuerbach, J. A. Piper, Macquarie Univ. (Australia)

Direct-write fabrication of guided wave devices using ultrafast lasers is a rapidly growing area of research. This fabrication platform can be readily applied to the creation of photonic devices such as low loss waveguides, splitters, Mach-Zehnder interferometers, 3D arrays and sensors. Most recently, ultrafast laser direct-write techniques have been applied to the fabrication of Bragg structures in both fibre [1] and bulk media [2,3]. This capability enables fabrication of a range of resonant photonic devices.

Bragg structures can be directly written with ultrafast lasers in one of 3 ways, namely using point by point inscription in an existing waveguide [1, 2], inscription of discrete voxels [3] or modulating the incident pulse energy whilst writing a waveguide [4]. Non direct-write methods using ultrafast lasers and a phase mask have also been demonstrated. In this presentation, methods for fabricating narrow line width Bragg structures in both fibre and bulk materials, and studies of direct-written optical resonators, will be reported.

1. A. Martinez, M. Dubov, I. Khrushchev and I. Bennion, *Electron. Lett.* 40, 1170 (2004).

2. G. D. Marshall, M. Ams and M. J. Withford, *Opt. Lett.* 31, 2690-2691 (2006).

3. H. B. Zhang, S. M. Eaton, J. Z. Li and P. R. Herman, *Opt. Lett.*, 31, 3495-3497 (2006).

4. G. D. Marshall, P. Dekker, M. Ams, J. A. Piper and M. J. Withford, postdeadline paper in OSA Topical Meeting on Bragg Gratings, Poling and Photosensitivity in glass waveguides (2007).

6879A-20, Session 7

Femtosecond laser direct writing of buried diffractive optical elements in fused silica

M. L. Ng, S. M. Eaton, D. Chanda, P. R. Herman, Univ. of Toronto (Canada)

Focused femtosecond lasers are now being extensively applied in modifying refractive index in glasses and other transparent materials for opportunities in creating 3-D optical circuits [1] and volume gratings [2]. With high repetition rate femtosecond lasers (0.1 to 1 MHz), fast writing speeds (>60 mm/s) have been demonstrated, which we extend, in this paper, to the fabrication of phase-contrast diffractive optical elements (DOEs) by high-resolution writing of 3D refractive index structures. Such buried 3D DOEs are inherently protected from surface damage and promise wider latitude in optical design due to the distributed 3D phase structures, which can not be easily achieved with traditional surface relief DOEs.

This paper reports direct laser writing of buried DOEs in fused silica (Corning 7980; $n = 1.457$) with a focused Yb-fiber amplified femtosecond laser (IMRA FCPA μ Jewel). Various laser repetition rates (0.1 to 1 MHz), focusing geometries (NA = 0.55 to 0.9) and laser exposure conditions have been explored to enhance refractive index contrast while minimizing the structure size. Near-field refractometry has been applied to assess refractive index contrast, structure size, and prospects for high resolution grating formation. Results of optimizing 1D volume gratings in fused silica will be presented together with a discussion of the tradeoff between resolution and refractive index contrast in forming submicron period gratings. Multi-layered stacks of crossed gratings have been developed that increase the grating efficiency and enable formation of multi-level two-dimensional diffractive optical elements. DOEs have been designed and laser fabricated that demonstrate controlled phase shifts between x- and y-oriented grating stacks for manipulating the symmetry of near-field interference patterns.