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Laurent Bigot, Hicham El Hamzaoui, Antoine Le Rouge, Géraud Bouwmans, Fernand Chassagneux, et al.. Linear and nonlinear optical properties of gold nanoparticle-doped photonic crystal fiber. Optics Express, 2011, 19 (20), pp.19061. 10.1364/OE.19.019061 . hal-00904095

**HAL Id: hal-00904095**
**https://hal.science/hal-00904095**

Submitted on 15 Nov 2013

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# Linear and nonlinear optical properties of gold nanoparticle-doped photonic crystal fiber

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**Abstract:** We report on the production of air/silica photonic crystal fiber doped with gold nanoparticles. The stack-and-draw technique was used to combine a gold nanoparticles-doped silica core rod synthesized by the sol-gel route with capillaries drawn from commercially available silica tubes. The presence of nanoparticles in the core region was confirmed at the different steps of the process down to the fiber geometry, even after multiple drawings at $\sim$2000 °C. Optical properties of the fiber were investigated and put in evidence the impact of gold nanoparticles on both linear and nonlinear transmission.

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**OCIS codes:** (060.5295) Photonic crystal fibers; (060.4370) Nonlinear optics, fibers; (160.4236) Nanomaterials.

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## 1. Introduction

The concept of photonic crystal fiber (PCF) has opened the route to a novel family of optical fibers available for a wide range of applications [1]. Among these fields, nonlinear optics took a large part of the benefits, making it possible to realize, for example, broad and powerful supercontinuum sources. The efficiency of these systems is based both on the easy chromatic dispersion management offered by PCFs and on the increased nonlinearity thanks to the small mode areas that are accessible with these fibers. The intrinsic nonlinear coefficients of the material generally plays a second role, as illustrated by the numerous realizations based on pure silica glass. However, various kinds of glasses are known to offer nonlinear coefficients larger than those of pure silica and could be useful to further improve the performances of systems based on highly nonlinear fibers. Roughly speaking, these glasses can be divided in two families: (1) nonlinear matrices, like chalcogenide glasses, multicomponent oxide glasses or tellurite glasses [2] and, (2) conventional glasses containing dopants that present nonlinear properties, like nanometric inclusions (metal, semiconductor) [3, 4]. Both kinds of materials have nonlinear coefficients significantly larger than those of pure silica and some of them have already been used to realize PCFs, like chalcogenide [5] and tellurite [6] for which the authors tried to exploit the high nonlinear-index coefficient. Besides this, realization of glasses doped by metal nanoparticles is mainly limited to films and bulk materials and there are only two reports of insertion of such systems in the core of a conventionnal optical fiber [7, 8]. However, it has been reported that these systems can also present high nonlinear-index coefficient and, in addition to this, high nonlinear-absorption coefficient that make them available for applications requiring saturable absorption or optical limiting [9]. In the case of gold nanoparticles (Au-NPs), the difficulty there exists in maintaining them in the core of an optical fiber originates from the high temperatures associated to fiber drawing. Such temperatures (typically $\sim$2000 °C for silica glasses) are much higher than the gold melting temperature (1064 °C) and even higher than Au-NP melting temperature [10]. The first report of an optical fiber containing Au-NPs was based on the evaporation of gold on a fiber end and the splicing to a second fiber [7]. The second work was based on conventional fiber fabrication technique (namely modified chemical vapor deposition) coupled to a solution doping technique using a gold precursor, similarly to what is done to realize rare-earth doped fibers [8]. Looking in details, it appears that the first approach can only lead to short doped pieces of fibers, whereas the results obtained with the second technique led to surprising properties: the reported surface plasmon resonance (SPR) wavelength is blue-shifted as compared to what is commonly reported for Au-NPs in silica.

In the present work, we propose to combine the benefit of the PCF geometry and the increased nonlinearity induced by Au-NPs to realize nonlinear silica fibers. In order to reach this goal, an alternative approach has been developed, based on the synthesis of a glass rod by a soft technique (namely the sol-gel route) and its use as core material for the realization of a PCF by the stack-and-draw technique. The crucial question of conservation of Au-NPs at the different steps of the process up to the fiber geometry is studied as well as the optical properties of the final fiber.

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## 2. Fiber synthesis

The first step of the fabrication consists in the synthesis of a cylindrical rod by the sol-gel route. This technique was chosen because it enables to achieve transparent glasses at temperature several hundreds degrees lower than the reaction temperature required in the conventional process used in the optical fiber industry. Porous silica monoliths, shaped as cylinders, were prepared from tetraethylorthosilicate (TEOS) as already described elsewhere [11]. Those porous monoliths, exhibiting interconnected nanometric pores, were doped by soaking with hydrogen tetrachloroaurate ($HAuCl_4$) solution. Then, the samples were taken out and dried for several hours so as to to remove solvents. The resulting doped xerogels were then densified under air atmosphere at 1200 °C and pink colored and cracks-free silica glass cylinders (few tens of millimeters in diameter and few centimeters in length - see inset of Fig. 1) were obtained. The absorbance is presented on Fig. 1.

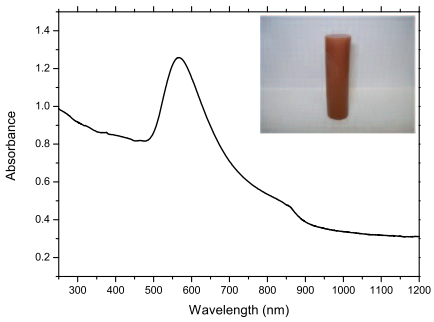


Fig. 1. Absorption spectrum of sol-gel Au-NPs -doped vitreous silica monolith. Inset: optical image of such a monolith.

It exhibits a broad resonance centered around 567 nm with a full width at half maximum (FWHM) of 117 nm, attributed to the SPR of Au-NPs. These Au-NPs were hence formed in the silica network during the drying and sintering of the sol-gel monolith. To obtain PCF, the sol-gel monolith presented in inset of Fig. 1 was jacketed with a pure silica tube and this set was then drawn down to millimeter-sized rods at around 2000 °C. The resulting rods also present a pink color which suggests the presence of Au-NPs at this step. This is confirmed by high-resolution transmission electronic microscopy (HR-TEM) and absorption measurement. Indeed, Au-NP of around 5 nm in diameter is observed as shown in Fig. 2, the metallic nature of this crystallite being confirmed by the inter-planar distances, which are close to the distances between (-111), (1-11) and (002) lattice planes of cubic face centered gold.

The SPR peak recorded on the millimeter-sized rod is roughly centered at the same wavelength as for the monolith. The observed resonance is red-shifted by 50 nm as compared to the wavelength generally reported for small Au-NPs in silica. We attribute this difference either to a particle size distribution centered on large diameters ($>$50 nm) or to the presence, confirmed by HR-TEM, of gold oxide around small Au-NPs. In this last hypothesis, the high refractive index of gold oxide could cause the observed red-shift [12,13]. Finally, it has to be pointed out that the amorphous nature of the silica matrix in which Au-NPs are embedded has been confirmed by Raman spectroscopy. These results put clearly in evidence that Au-NPs can be preserved, even after such a high temperature process. The jacketing/drawing procedure was repeated two more times in order to get millimeter-sized rods with only their central part doped with Au-NPs. The

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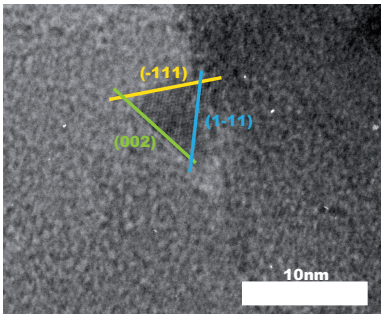


Fig. 2. HR-TEM image realized on a rod directly drawn from a monolith.

aim of this process was to adjust the overlap between the guided mode and the doped region in the resulting fiber. This method allowed us to reduce the strong Au-NPs -related absorption, thus facilitating absorption measurements. The final rods were stacked with pure silica capillaries in a hexagonal arrangement. The stack was then placed inside a silica jacket tube and drawn down to cane, itself placed inside a silica jacket tube and finally drawn down to fiber. The Au-NPs -doped material has hence been heated five times at $\sim$2000 °C before reaching the fiber geometry. Scanning electron microscope (SEM) image of the central region of the fiber is presented in inset of Fig. 3, together with a schematic representation of the Au-NPs -doped region whose diameter is around 460 nm. The geometry of the fiber is the following: the outside diameter is $\sim$125 $\mu$m, the pitch of the periodic cladding, $\Lambda$, and the diameter of the air holes, $d$, are $\sim$3.9 $\mu$m and $\sim$1.6 $\mu$m, respectively. These values lead to a ratio $d/\Lambda$ below 0.42 so that fiber can be considered as endlessly singlemode [1].

## 3. Optical properties

Optical attenuation of the fiber was measured by the conventional cut-back technique using a supercontinuum source (Fianium SC-400) and an optical spectrum analyzer (ANDO 6315). Two different initial fiber lengths were used in order to accurately measure both background losses and Au-NPs -related SPR.

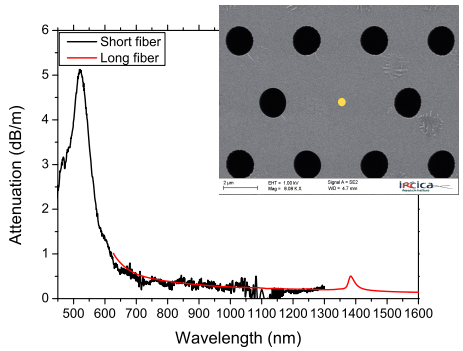


Fig. 3. Optical attenuation of the Au-Nps -doped PCF measured by cutting back two different initial fiber lengths: 50 m (red line) and 2 m (black line). Inset: SEM image of the central part of the PCF. Au-NPs -doped region has been schematized by a yellow circle.

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SPR absorption of ∼5 dB/m is clearly observed at ∼522 nm for the obtained fiber (Fig. 3), with FWHM of 108 nm. Background losses in the near infrared region are around 140 dB/km for this fiber. As compared to the results published by Ju et al. [8], the observed SPR correlates much better with what is known for spherical Au-NPs of a few nanometers in diameter, embedded in silica matrix [14]. It has to be underlined that the apparent small Au-NPs -related attenuation is only due to the weak overlap (estimated to 1.5 %) between the guided mode and the doped region. Taking this into account, the results suggest that the effective absorption of the doped region is larger than 300 dB/m. In order to evaluate the impact of Au-NPs on the nonlinear optical properties, the evolution of the transmission of fiber was measured as a function of the input power at 532 nm. Hence, a 1064 nm sub-nanosecond microchip laser (Teem Photonics NP-10820-100) was frequency-doubled using a PP-KTP crystal and then injected into about 1.6 m of the fiber under investigation. Input and output powers were measured using a powermeter. So as to focus on the sole impact of Au-NPs doping, Au-Nps -doped PCF was compared to an undoped PCF having a pure silica sol-gel -based core, similar geometry and same length. The results are presented on Fig. 4 for both fibers for which mode effective areas and coupling coefficients have respectively been measured and calculated in order to estimate input/output intensities. Whereas a linear dependence is observed for the pure silica sol-gel PCF, Au-NPs -doped PCF presents a singular behavior characterized by the sub-linear evolution of output intensity versus injected intensity. This optical limiting effect is attributed to the presence of Au-NPs. It has to be noted that, in both cases, the obtained results were reversible as a function of the input intensity.

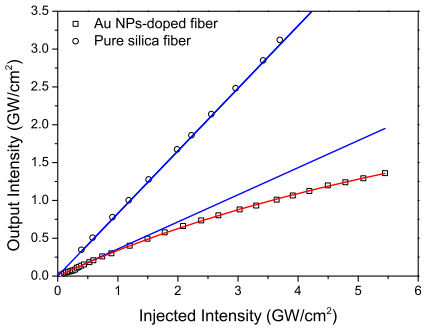


Fig. 4. Evolution of output intensity as a function of input intensity, at 532 nm, for two different optical fibers: undoped sol-gel -based pure silica core micro-structured fiber (open circles) and Au-Nps-doped fiber presented on Fig. 3 (open squares). In both cases, a linear fit of the first experimental data points is represented by a blue line. A fit of the experimental data points obtained for Au-NPs -doped PCF based on Eq. (2) is reported as a red line.

In order to further characterize the nonlinearity of the Au-NPs -doped PCF, the following law was used to describe the intensity dependence:

$$\frac{dI}{dz} = -(\alpha I + \beta I^2) \tag{1}$$

The solution of Eq. (1) for the transmitted intensity $I(L)$ in a fiber of length $L$ is given by:

$$I(L) = \frac{I(0)e^{-\alpha L}}{1 + I(0)\beta L_{eff}} \tag{2}$$

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where $I(0)$ stands for the injected intensity, $\alpha$ stands for the low-intensity absorption coefficient, $\beta$ stands for the induced absorption coefficient (two-photon absorption coefficient for example) connected to the imaginary part of the third order susceptibility [15] and $L_{eff} = \frac{1-e^{-\alpha L}}{\alpha}$ is the effective length. A fit by Eq. (2) leads to a value of the $\beta$ coefficient of $0.84\times10^{-12}$ cm/W for the Au-NPs -doped PCF. The relatively small apparent value obtained for $\beta$, as compared to reports on Au-NPs -doped films [14], is attributed to the weak overlap between the guided mode and the doped region, together with the much smaller Au-NPs concentration when compared to what is commonly presented in the case of films. The resonant optical limiting behavior observed in the obtained fiber, can be correlated to the excited-state absorption of carriers in the Au-NPs and the generation of hot electrons.

## 4. Conclusion

In conclusion, we report on the production of PCFs with core realized by the sol-gel technique and doped with Au-NPs. Preservation of Au-NPs all along the fiber manufacturing process is demonstrated and SPR is clearly observed, even for the fiber geometry. The effect of this doping on the resonant nonlinear properties of the fiber is put in evidence and is characterized by an optical limiting effect. We hope that this optical limiting behavior could be extended to the non-resonant region, opening perspectives for clamping energy of lasers or amplifiers.

## Acknowledgments

The authors would like to thank Karen Delplace for providing technical support. This work has been performed in the frame of the POMESCO ANR project. It has also been partly supported by the Conseil Régional Nord/Pas de Calais and the Fonds Européen de Développement Economique des Régions (FEDER).

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