Second-harmonic generation from green printed selenium structures

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Abstract.
Plenary large-scale efficient second-harmonic generation sources remains a challenge in micro-/nanoscale research. In this work, we demonstrate the strong second-harmonic generation in arrays of selenium particles fabricated by green printing method at the pumping wavelength of 1047 nm. Second-harmonic generation mapping shows the strong signal over the whole area of selenium particle. We propose, that such structures can be a perspective platform for efficient frequency conversion systems and nonlinear sensing applications.

1. Introduction
Creation of frequency conversion systems at micro- and nano-scales plays an important role in modern photonics and optics. Particular interest lies in the fabrication of second-harmonic generation (SHG) sources which can be utilized for laser spectroscopy application [1], data recording, sensing [2] etc. For producing such structures, a variety of different methods are used: chemical [3], lithography [4], thermal [5] and many others. Green printing is a new and promising method for this goal due to its low cost, environmental friendliness and simplicity [6]. For instance, micro-/nanoscale pattern can be formed by micropillar array templates induced self-assembly of particles or deposited films. This method requires materials with deposition control and relatively low melting point [7]. One of suitable materials for this goal is selenium. Selenium is a semiconductor with a high refractive index and extremely low losses in the visible range that makes it an ideal system for providing interesting optical effects on printed micro- and nanoparticles [8].

In this work we produce arrays of selenium particles on silicon substrate by green printing method. We observe, that such particles exhibit a strong second-harmonic generation signal at the visible range. We propose that produced structures have a big potential for nanophotonic systems and devices.

2. Materials and methods
2.1. Se array fabrication
At the first step, polydimethylsiloxane (PDMS) template is replicated from the prepared Si groove shape stamp with width of grooves \( w = 10 \mu m \), height \( h = 20 \mu m \) and period \( p = 20 \mu m \) (see Fig. 1a). Firstly, 2 g of selenium power is loaded in the evaporation boat. Selenium film is evaporated on the PDMS template at the rate of 0.1 nm/s for a thickness of 2 \( \mu m \) for fluid-guided printing (see Fig. 1b). Then
the silicon substrate is covered by the PDMS template with selenium, and the fluid-guided printing is conducted at 100 °C. During this process, the selenium particles are printed on the substrate due to the Rayleigh instability (see Fig. 1c). Finally, the template is uncovered after cooling down to the room temperature and arrays of Se particles on silicon substrate are printed (see Fig. 1d).

**Figure 1.** Green printing process. a) Creation of PDMS template by stamping from the groove-shaped silicon substrate; b) Se evaporation on the template; c) Narrowing and shaping of Se with the guidance of template; d) Printed Se particle arrays

2.2. Geometry characterization
External geometry characterization of structures with high accuracy was provided by Scanning Electron Microscopy (SEM). SEM images of the studied structures were obtained by Inspect (Field Electron and Ion Company, FEI) system in vacuum chamber under pressure $10^{-3}-10^{-4}$ Pa and accelerating voltage 20 kV in mode of secondary electrons detection.

2.3. SHG signal measurements
SHG signal of the selenium structures were excited under the pumping of a femtosecond (fs) oscillator TEMA-150 (Avesta Project) generating at a wavelength of 1047±5 nm (pulse duration = 150 fs, repetition rate = 80 MHz). Laser beam was focused on the structures from the top by Mitutoyo Plan Apo NIR HR objective (100x, NA = 0.7). Excited SHG signal was collected by the same objective and directed to spectrometer Horiba LabRam HR800. The sample was placed on a piezo stage (AIST NT) with positioning accuracy of 10 nm during the two-dimensional mapping of SHG signal.

3. Results and discussion
Arrays of selenium particles on silicon substrate are fabricated by the green printing method which was proposed in [6]. SEM imaging is performed to investigate the configuration of the printed structures. SEM images of the whole structure and zoomed top and side images of a selenium semi-sphere are illustrated in Fig. 2. As it can be seen from Fig. 2a, the distance between each row is set to be 20 µm which is in a good agreement with period between grooves on Si stamp. The typical width and length of structures are 1-2 µm and several µm, respectively. It should be noted, that the width of the selenium array is determined by the evaporation procedure in Fig. 1b. For investigation of nonlinear properties, we choose the Se particle with a diameter around 1.2 µm which is indicated by a white dashed box in Fig. 2a and its magnified top view and side view SEM images are shown in Fig. 2b and Fig. 2c, respectively.

Measured SHG spectrum from the chosen particle is depicted in Fig. 3a. From the figure it can be observed, that fabricated Se structure generates quite strong SHG signal at the double frequency of the
Figure 2. Geometry characterization of Se structures. a) SEM image of array; b) Top and c) side view of chosen area defined by white dashed box in a)

fundamental laser excitation. To investigate SHG intensity distribution over the Se particle area, a SHG map is recorded with a step size of 80 nm utilizing piezo stage (Fig. 3b). As it can be seen from the figure, the SHG signal is strong over the whole area of the particle. Thus, produced arrays of Se structures can be used as efficient SHG sources.

Figure 3. Measured nonlinear signal. a) SHG signal collected from one particle; b) SHG map of Se particle at the double frequency of the laser (524 nm)

4. Conclusion
In summary, we have fabricated Se arrays composed of microparticles on silicon substrate by the green printing method. These structures demonstrate strong SHG signal during irradiation by the beam of a fs-laser at the wavelength of 1047 nm. The SEM image presents homogeneous configuration of the Se particle. The SHG map provides strong signal over the Se particle area which demonstrates high potential in promising large-scale planar SHG source. Proposed green printing method can be applied for fabrication of both micro- and nanarrays made of selenium which makes it a promising platform for creation of efficient nonlinear sensors and frequency conversion systems.
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