

# Formation and selective micron-region control of PbS quantum dots inside glasses using femtosecond laser pulses

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## 1. Experimental Section

**Preparation of the glasses:** The two kinds of glass samples used in our experiment were both prepared by the melting-quenching technique. Initially, the glasses without AgNO<sub>3</sub> (NAG) were prepared using the following composition: 66SiO<sub>2</sub>-8B<sub>2</sub>O<sub>3</sub>-18K<sub>2</sub>O-6ZnO-1ZnS-1PbO (in mol %). The mixture of analytical grade raw materials SiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, ZnO, ZnS and PbO were melted at 1450 °C in an alumina crucible for 90min under ambient conditions, quenched in a preheated brass mold and annealed at 400 °C for 1 h. As to the other kind of glass, when melting extra 20 ppm (in mol %) AgNO<sub>3</sub> (AG) was added in compared to the first kind of glass and the fabrication process is the same with the glass without AgNO<sub>3</sub>.

**Heat-treatment of the as-prepared glasses and its characterizations:** The as-prepared two kinds of glasses both with slight yellow color were cut and further annealed at 540 °C, 560 °C and 580 °C for different durations. After heat treatment, the samples were cooled to room temperature inside the furnace and then polished into a plate of 1 mm thick to make further characterizations. The photoluminescence spectra were measured on a Triax 320 spectrometer (Jobin-Yvon Co., France) with a resolution of 1 nm, which were excited by a 976 nm laser diode (LD) and detected with a PbSe photodetector. Optical transmittance spectra of glass composites were recorded on a UV/VIS/NIR spectrophotometer (Lambda-900, Perkin-Elmer, USA). The confocal Raman spectra from the heat treated samples with a 785 nm laser as the excitation source were measured by a

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Raman spectrometer (Renishaw inVia). The morphology and crystallization of PbS QDs in glasses were characterized by high-resolution transmission electron microscopy (HR-TEM; Philips-FEI, 5 The Netherlands). The HR-TEM sample was prepared by placing a drop of a dilute glycol dispersion of the glass powder on the surface of a copper grid and then dried at room temperature. All the measurements were carried out at room temperature.

***Micro-region controlled precipitation of QDs using fs laser and subsequent heat-treatment***

***regulation:*** The two kinds of glass samples were irradiated by fs laser pulses at ambient atmosphere under the same condition. A commercial femtosecond Yb-fiber laser system (FLCPA-02USCT11, Calmar Laser) was used to produce femtosecond laser pulses with central wavelength of 1030 nm, pulse duration of 370 fs, and repetition rate of 500 kHz. The laser pulses were focused at 150  $\mu\text{m}$  beneath the glass surface via a microscope objective (50 $\times$ , NA=0.8). The irradiated region was manipulated by a three-dimensional XYZ stage with a precision of 100 nm controlled by a computer. Three average powers (1.2 W, 1.5 W and 1.8 W) were selected to precipitate the quantum dots in the glass samples. By using an XYZ stage controlled by a computer, the laser focus was moved up from 150  $\mu\text{m}$  to 50  $\mu\text{m}$  beneath the glass surface at rates of 5  $\mu\text{m}/\text{s}$  and 10  $\mu\text{m}/\text{s}$ , respectively. There were no microcracks were observed at the high-repetition femtosecond laser irradiated regions, indicating a generation of smooth region with change of refractive index. Then the samples characterized with the confocal Raman spectra and the Raman Mapping was also conducted. Additionally, we measured the characteristic radiation from the area irradiated with ultrashort laser pulses on the cross-section by electron probe micro analyzer (EPMA: EPMA-1600, Shimadzu). Selective micron-region (diameter:  $\sim 30 \mu\text{m}$ ) control of PbS QDs is realized in the glass matrix. On the other hand, the irradiated  $\text{AgNO}_3$  doped glasses were also annealed at 540  $^\circ\text{C}$  for 5 h and 7.5 h to investigate the formation and growth of PbS QDs. After annealing, the samples were still transparent with a yellow color but a bit of darker than the as-prepared counterparts. Heat treatment of the irradiated area shows that the photoluminescence band of the QDs can be regulated from  $\sim 800 \text{ nm}$  up to  $\sim 1100 \text{ nm}$ . In the whole process, it is demonstrated that the formation of the

QDs can be precisely controlled in the irradiated micron-region without the formation of QDs in the non-irradiated glass matrix.

**Waveguide Demonstration:** An amplified Ti:sapphire laser system (150 fs, 800 nm, and 1 kHz repetition rate) system was used to inscribe waveguide in the glass doped with AgNO<sub>3</sub>. The fs laser was focused into the samples approximately 200 μm below the surface by a microscope objective (20×, NA=0.45). Pulse average power 10 mW was used in the formation of optical waveguides. The sample was moved perpendicular to the laser-beam axis by a computer-controlled positioning system with a velocity of 20 μm/s during the writing process. The end-face coupling method was used to characterize the transmission properties of channel waveguide. The polarized light beam at the wavelength of 632 nm was coupled into the waveguide by a 10× microscope objective lens to excite the guide modes. And at the output facet of the sample, the output light was collected using another 50× microscope objective lens, then imaged onto a CCD camera. Therefore, we obtained the near-field intensity distributions of waveguide structures.

## **2. Discussion about the migration of Si, O, K, Zn and B.**

Group I ions known as network formers form the framework of the glass sample and group II ions known as network modifiers provide additional oxygen ions that modify the network structure. The single-bond strength of the network formers Si–O (106 kcal/g atom) is much higher than that of the network modifiers, taking K–O (13 kcal/g atom) for example [1]. Therefore, the bonds of the network modifiers will be easily broken, and each ion will diffuse away from the focal point.

Koubassov et al. suggested the possibility of melting and subsequent structural change at the focal point in SiO<sub>2</sub> glass during fs laser irradiation [2]. When the fs laser beam was focused inside a glass, it ruptured at the focal point and transformed into a liquid state, then, all the bonds linking the metallic ions broke, resulting in the dispersion of the ions with a ring shape. In addition, diffusion classified as multicomponent diffusion occurred during laser irradiation because the sample glass contained many additional species classified as Group II ions. Since the diffusion coefficient of

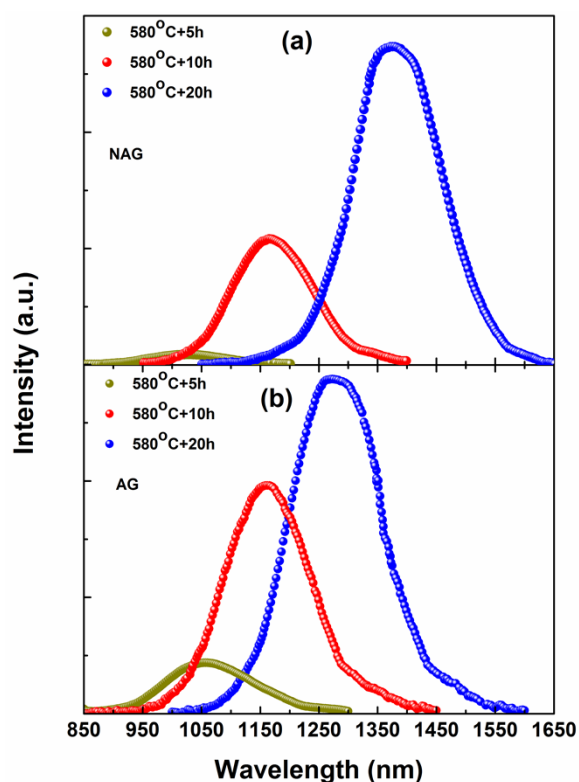
various modifiers (group II ions) was generally larger than that of the group I ions, group II ions diffused away from the laser-irradiated area due to the generation of shock waves and migrated out of the melting zone, thereby producing a ring [3].

### 3. Table S1

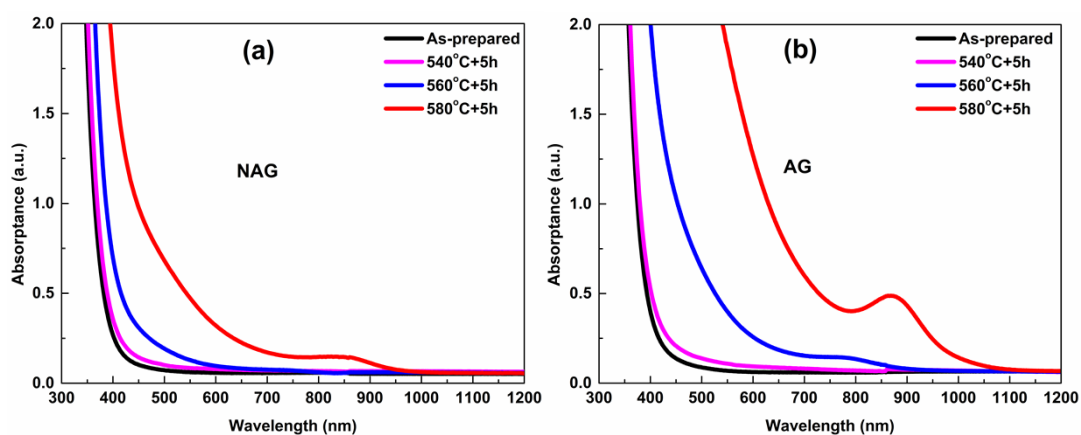
Table 1. Absorption peak position ( $\lambda_{\text{abs}}$ ), absorption coefficient ( $\alpha$ ), and calculated average radius (R) of PbS QDs precipitated in glasses with 0 and 20 ppm  $\text{AgNO}_3$  by heat-treatment for different durations at 580 °C.

Treatment duration (h)	$\lambda_{\text{abs}}$ (nm)		$\alpha(\text{cm}^{-1})$		R(nm)	
	0	20 ppm	0	20 ppm	0	20 ppm
3	787	804	0.15	0.29	1.49	1.52
5	850	874	0.18	0.50	1.62	1.67
10	1067	1039	0.34	0.83	2.08	2.02
20	1330	1192	0.75	1.30	2.71	2.37

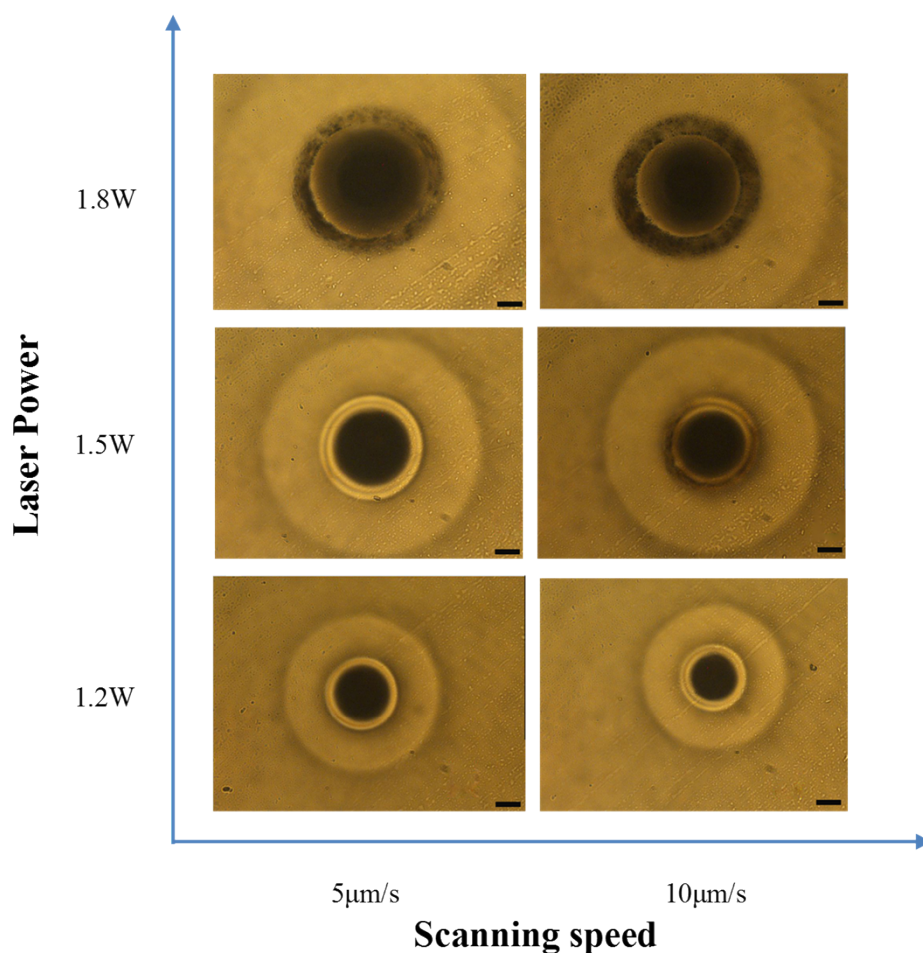
### 4. Figure S1-S4



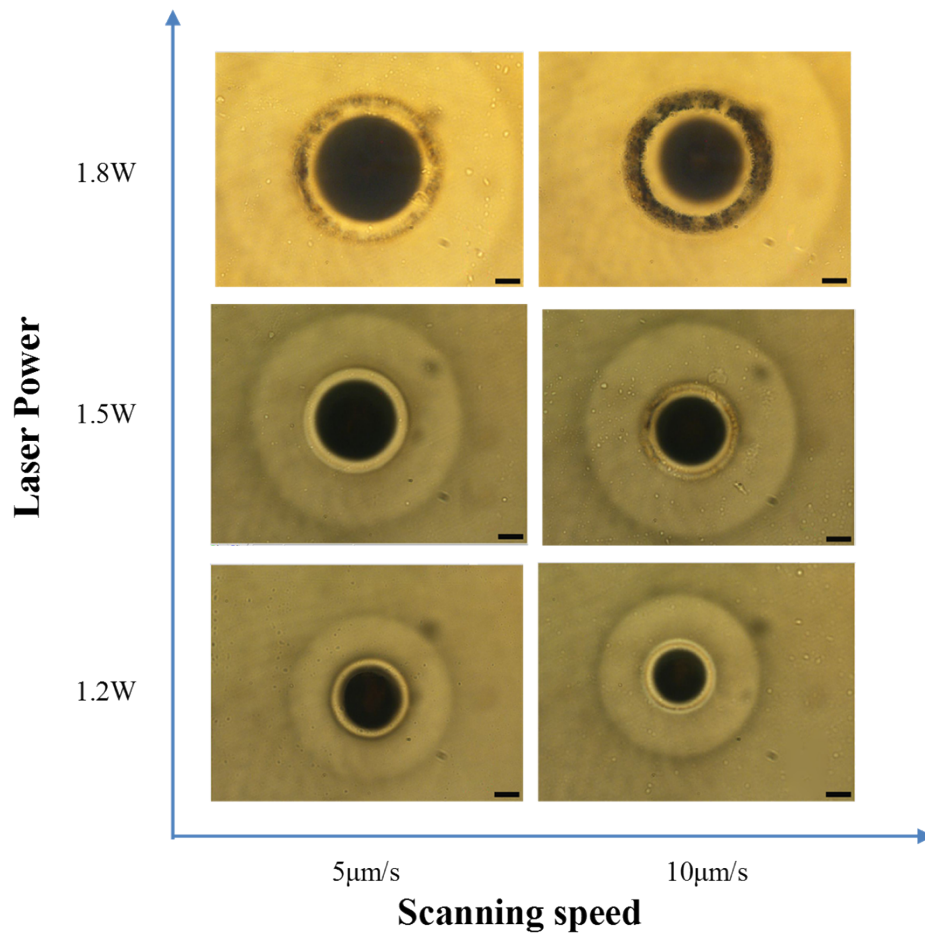
**Figure S1** Photoluminescence spectra of glasses doped without  $\text{AgNO}_3$ : NAG (a) and with  $\text{AgNO}_3$ : AG (b) heat treated at 580 °C for different durations under 980 nm laser excitation.



**Figure S2** Absorption spectra of NAG (a) and AG (b) heat treated at different temperatures for 5 hours.



**Figure S3** Optical microscope images for NAG after irradiated with different laser power and scanning speed. All of the scale bars in the pictures represent 20 μm.



**Figure S4** Optical microscope images for AG after irradiated with different laser power and scanning speed. All of the scale bars in the pictures represent 20  $\mu\text{m}$ .

### References

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