Laser damage resistance of polystyrene opal photonic crystals

Lei Pan1, Hongbo Xu1, Ruizhen Lv2, Jun Qiu3, Jiupeng Zhao1 & Yao Li2

The laser damage behavior of three-dimensional photonic crystals (3D-PCs) with an opal structure is investigated using both experimental and simulation methods. Polystyrene (PS) colloidal crystals films with a reflection peak at 1064 nm are used as the model material. Disordered films (DF) are fabricated with PS microspheres as contrast samples. The laser-induced damage threshold (LIDT) of 3D-PCs is tested, which is as 2.35 times high as the LIDT of DF. All laser damages are derived from defects in 3D-PCs, implying that the LIDT of ideal 3D-PCs will be significantly increased. The simulation results show that the electric field is contained in the pores of 3D-PCs while it is reduced in the PS microspheres, which may decrease the absorption of laser energy by 3D-PCs. In contrast, the electric field distribution is irregular in DF. Enhanced electric field areas are located in both the pores and microspheres of DF. Considering higher electric field intensity causes more energy absorption and higher temperature, the DF have a lower LIDT. The 3D-PCs structure uses ordered vacancy to contain and strike back laser energy and can increase the LIDT without changing the chemical composition of materials.

Photonic crystals (PCs) are a class of artificial materials with photonic band gaps (PBGs) that originate from their periodic dielectric structures1. Many laser-related applications of PCs are being proposed or demonstrated, such as all-optical circuits2, omnidirectional reflectors3, high power laser applications4, high-Q nanocavity lasers5,6, and low-threshold lasers7–9, owing to its ability to manipulate light. For a versatile tool to generate and manipulate laser, laser-induced damage threshold (LIDT) of PCs is a key property that decides the whole performance10.

Traditional optical coatings such as high reflection coatings, anti-reflection coatings, and beam splitters are composed of periodic dielectric films and can be regarded as one-dimensional PCs (1D-PCs). The origin, nature, and characteristics of the LIDT of 1D-PCs have been extensively studied10–17. Contamination and structural defects give rise to most failures in 1D-PCs10,16 and lead to a much lower LIDT than the LIDT of bulk materials.

PBG fiber, a kind of two dimensional PCs (2D-PCs), attracted attention as candidates for the transport of very high power laser pulses recently18. It is reported that a PBG fiber carries most of the transmitted power in its hollow core and as little as 0.2% of the energy in the silica19, which results in a LIDT representing an order of 4 improvement compared to solid-core photonic crystal fibers20. Similar results are reported for two dimensional periodic arrays of nano-horns as anti-reflection layers21–24. The chalcogenide glass with 2D-PCs shows almost a factor of 2 improvement in the LIDT compared to untreated bulk glass22 mainly because no foreign material is introduced24. The strong electric field region for 1064 nm laser is distinctly distributed in the hollow part of the periodic array, which may also promote the LIDT21.

Three dimensional ordered25,26 and disordered25,27,28 nano-structures were also manufactured for high power laser applications. Li et al. observed a slightly higher LIDT in ordered porous silica coating than in the disordered one25. Despite the difference in absorption, the authors believe that the ordered structure is the key to interpret the high LIDT. However, Du et al. argued that for a small period-to-wavelength ratio, electromagnetic fields do not vary spatially and the periodicity of nanostructures would be less important to their performance27. In this sense, the ordered nanoporous coating was not a typical photonic crystal for the laser used in the testing. High LIDT was reported for three dimensional disordered nanoporous antireflective coatings as well and the influence of orderliness on LIDT was not discussed27,28.

An interesting result can be found if one compares the LIDT investigation of 1D and 2D photonic crystals, despite different testing methods, materials, and substrates, the LIDT of 1D-PCs is generally much lower than that of the substrates10–17 while the LIDT of 2D-PCs is close to or higher than the LIDT of substrates or bulk

1MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin, 150001, China. 2Center for Composite Materials and Structure, Harbin Institute of Technology, Harbin, 150001, China. 3School of Energy Science and Engineering, Harbin Institute of Technology, Harbin, 150001, China. Correspondence and requests for materials should be addressed to J.Q. (email: qiujun@hit.edu.cn) or J.Z. (email: jzpzhao@hit.edu.cn) or Y.L. (email: yaoli@hit.edu.cn)
Many reasons may underlie this result, the ways by which the two kinds of ordered structures were constructed being one of them. 1D-PCs must consist of at least two dielectric materials (both solid usually) layer by layer and laser needs to propagate through them in sequence. The layer with the lowest LIDT, which may be defined by its chemical nature, contamination, or defects in the interface, will be the shortest stave in the barrel. However, in the 2D-PCs, the second dielectric material is usually a vacancy (air or vacuum) whose LIDT is much higher than all solid materials. Besides, the manner in which laser passes through the 2D-PCs may be different from 1D-PCs. By elaborately designing the arrangement of solid material, the bulk of laser energy can be confined within the vacancy to avoid the damage of the solid part such that the LIDT of the whole 2D-PCs is promoted. This mechanism accords with the old Chinese philosophy that vacancy makes tools more useful (Tao-te-ching, chapter 11, about 500BC).

Vacancies exist in 3D-PCs as well; however, solid materials in three dimensions baffle them periodically. Until now, the influence three-dimensional ordered structures with periods falling in the range of laser wavelength exert on the LIDT was unknown. Hereby we carried out experimental and simulative research on this problem.

**Results and Discussion**

**Experiments results.** Among the various preparation methods for 3D-PCs, self-assembly of PS microspheres is most widely used, as it is convenient and low cost. Moreover, the low melting point of PS is in favor of the LIDT test. Hence, we choose PS 3D-PCs to conduct the laser-induced damage investigation. To format a pseudo band gap centered at 1064 nm, the average diameter of PS microspheres was carefully adjusted to 465 nm. The PDI of the diameter was 1.04. PS 3D-PCs were grown on glass slides by vertical deposition. The SEM images of PS 3D-PCs are shown in Fig. 1. It is observed in the Fig. 1a that the deposited PS 3D-PCs have a well-ordered nano-architecture consisting of close-packed spheres. However, as shown in Fig. 1b, point defects and planar defects also exist in a larger range.

The experimental reflectance spectrum of the PS 3D-PCs is given in Fig. 2. A reflective peak near 90% can be found for PS 3D-PCs in Fig. 2, whose location is very close to the wavelength of Nd:YAG laser, indicating the highly ordered structure of the PS 3D-PCs.

**LIDT test.** An Nd:YAG laser with a wavelength of 1064 nm was used as laser source for the LIDT test in continuous wave mode. The 1/e² spot diameters measured via the knife-edge method were 3.0 mm and the effective spot sizes were 7.1 mm². The beam of laser was collimated instead of focused because the high power density is not necessary for the damage of PS.
that in the vacancies, which is obviously beneficial to elevate the LIDT of the entire film. The ordered vacancies
distributed in the vacancies among PS microspheres, and the EFI inside the PS microspheres is significantly lower than
the EFI in PS microspheres. It is immediately noticed that the DEF in 3D-PCs is highly ordered. The EFI is mainly distrib-
uted in the x-z plane, where y = 0 and y-z plane, where x = 0, respectively. Black lines highlight the boundaries
of PS microspheres. It is immediately noticed that the DEF in 3D-PCs is highly ordered. The EFI is mainly distrib-
uted in the vacancies among PS microspheres, and the EFI inside the PS microspheres is significantly lower than
that in the vacancies, which is obviously beneficial to elevate the LIDT of the entire film. The ordered vacancies
are positively related to the EFI. Therefore, it is necessary to investigate the DEF in 3D-PCs for further interpreting
the mechanism of laser damage. Absorption of laser is a source of electromagnetic field disturbance, causing micro-focus effect and leading to the damage of materials. The fact that laser damages of 3D-PCs are derived from defects further implies that if the defects could be effectively
removed, the LIDT of perfect 3D-PCs would be significantly increased. Moreover, it can be speculated reasonably
that the redistribution of electromagnetic field caused by the ordered structure of 3D-PCs neither gives rise to
the harmful micro-focus in the PS microspheres lattice nor promotes the melting of PS like disordered structures.Near-field simulation will be employed to prove this speculation. The morphology of DF before irradiation is exhib-
ted in Fig. 4g. Microspheres are piled together in a jumble as expected. Homogeneous melting occurs in the DF
under laser irradiation and aggravates uniformly with the time, as noted from Fig. 4h and i.

**Simulation.** Various investigations showed that the LIDT of optical materials is closely related to the elec-
tric field intensity (EFI) in the materials and the distribution of the electric field (DEF) throughout the materi-
als is taken as an indication of susceptibility to damage. This is because although the materials used in these
researches are almost transparent, very small but non-negligible absorptance for laser still exists owing to impu-
rities, which gives rise to thermal effect and is responsible for most laser induced damages. Absorption of laser is
positively related to the EFI. Therefore, it is necessary to investigate the DEF in 3D-PCs for further interpreting
how ordered structures affect the LIDT of materials. The DEF intensity of 3D-PCs and DF was simulated numeri-
cally using finite-difference time-domain method.

The unit cell of both 3D-PCs and DF were designed in rectangle lattices, as illustrated in Fig. 5a and b, respecti-
vely. Periodic boundary conditions were set around a unit cell, while perfectly matched layer absorbing bound-
ary conditions were used at the top and bottom boundaries of the cell. The incidence optical source was set as
unpolarized plane waves at normal incidence.

The reflective spectrum of 3D-PCs was simulated using a source with a wavelength range from 700 nm to
1800 nm and was plotted in Fig. 2. The position of the reflective peak agrees well with the experimental result.
The DEF was simulated using a source with a wavelength at 1064 nm. Figure 6a and b depict the normalized DEF
images of the x-z plane, where y = 0 and y-z plane, where x = 0, respectively. Black lines highlight the boundaries
of PS microspheres. It is immediately noticed that the DEF in 3D-PCs is highly ordered. The EFI is mainly distrib-
uted in the vacancies among PS microspheres, and the EFI inside the PS microspheres is significantly lower than
that in the vacancies, which is obviously beneficial to elevate the LIDT of the entire film. The ordered vacancies

![Figure 3. LIDT for PS 3D-PCs and DF.](image-url)
firstly contain the energy of laser without damaging the material and then reflect it backwards. This principle is similar to the traditional Shadow Boxing conceived from Tao-te-ching, which fights back the strongest strike with nothing. Besides, it can be seen that the EFI is rapidly attenuated due to the pseudo forbidden band in the

**Figure 4.** SEM images of 3D-PCs with a pseudo band gap at 1064 nm (a–f) and DF (g–i) before or after 1064 nm laser irradiation. (a) The whole irradiation spot on 3D-PCs, (b–e) different defects after irradiation, (f) severely melted 3D-PCs, (g) DF before irradiation, (i) lightly melted DF (h), severely melted DF.

**Figure 5.** Simulation unit of (a) 3D-PCs and (b) DF. 3D-PCs consist of 9 layers of PS microspheres in opal structure. DF consist of random distributed PS microspheres. Periodic boundary conditions were set around a unit cell, while perfectly matched layer absorbing boundary conditions were used at the top and bottom boundaries of the cell.
z-direction; the EFI in the upper most level, both inside and outside the microspheres, is the highest, which is consistent with the results that the first-level microspheres melt the most, as shown in Fig. 4e.

On the contrary, the DEF of disordered PS microsphere films is very disordered and nonuniform, as illustrated in Fig. 6c. Owing to the “micro-focus” effect of disordered structures, the highest EFI is almost 4 times that of the source. In addition, the “micro-focuses” locate randomly both in vacancies and PS microspheres. The average EFI inside the microspheres of disordered PS films is significantly higher than that of 3D-PCs, which naturally leads to higher absorption and lower LIDT. Besides, laser propagates through the disordered PS film without evident attenuation.

Methods

All reagents except water used were commercial Sigma-Aldrich products. High-purity water with a resistivity of 18.2 MΩ·cm at 25 °C was prepared by a water purification system (CSR-1-30T).

Monodisperse polystyrene (PS) microspheres were synthesized by an emulsifier-free emulsion polymerization technique. Scanning electron microscopy (SEM) images were obtained using a Hitachi SU 8000 microscope operated at 15 kV. The average diameter of the PS microspheres was calculated from more than 100 microspheres. Polydispersity index (PDI) = Dm/Dn − 1, where Dm and Dn were the weight-average and number-average diameters, respectively. The normal-incident reflectance spectra of 3D-PCs were obtained by using an Ocean Optics NIR Quest instrument equipped with a reflection probe. A specular reflectance standard (PNA338–MS-1) with a reflectance of 85–90% was used as measured reference.

An Nd:YAG laser was used as a laser source for LIDT test on continuous wave mode. The 1/e2 spot diameters measured via the knife-edge method were 3 mm and the effective spot sizes were 7 mm2.

Conclusions

PS 3D-PCs with a pseudo forbidden band centered at 1064 nm were prepared by vertical deposition. The LIDT of 3D-PCs is 2.35 times high as the LIDT of DF fabricated with the same material. The laser damages of 3D-PCs are derived from defects. The simulation results show that the ordered structure of the 3D-PCs plays a very interesting role of modulating the DEF of laser. The EFI is mainly contained in the vacancies among microspheres during its short propagation in 3D-PCs and the EFI inside the microspheres is significantly lower than that outside. Besides, the EFI rapidly decreases with the increase of penetration depth in 3D-PCs. Such a DEF is very conducive to preventing laser damage. In contrast, “micro-focuses” with high EFI locate randomly both in vacancies and PS microspheres in DF. This explains the higher LIDT of 3D-PCs than DF. The laser damages observed in the experiment are derived from a variety of defects. Therefore, it can be reasonably speculated that ideal flawless opal photonic crystals will have a much higher LIDT.

In short, 3D-PCs structure uses ordered vacancy to contain and strike back laser energy and can increase the LIDT without changing the chemical composition of materials.

References

1. Yablonovitch, E. Inhibited spontaneous emission in solid-state physics and electronics. Phys. Rev. Lett. 58, 2059–2062 (1987).
2. Joannopoulos, J. D., Villeneuve, P. R. & Fan, S. Photonic crystals: putting a new twist on light. Nature 386, 143–149 (1997).
3. Zhang, H., Liu, S., Kong, X., Bian, B. & Dai, Y. Omnidirectional photonic band gap enlarged by one-dimensional ternary unmagnetized plasma photonic crystals based on a new Fibonacci quasiperiodic structure. Phys. Plasmas 19, 112102, https://doi.org/10.1063/1.4765063 (2012).
4. Benoit, F. et al. In Nanoengineering: Fabrication, Properties, Optics, and Devices XII. (eds Campo, E. M., Dobisz, E. A. & Eldada, L. A.) (Spie-Int Soc Optical Engineering).
5. Akahane, Y., Asano, T., Song, B. & Noda, S. High-Q photonic nanocavity in a two-dimensional photonic crystal. Science 284, 1819–1821 (1999).
6. Furumi, S., Fudouzi, H., Miyazaki, H. T. & Sakka, Y. Flexible polymer colloidal-crystal lasers with a light-emitting planar defect. Adv. Mater. 19, 2067–2072, https://doi.org/10.1002/adma.200602835 (2007).
9. Zhong, K. et al. Defect Mode Passband Lasing in Self-Assembled Photonic Crystal. *Acs Photonics* 3, 2330–2337, https://doi.org/10.1021/acsphotonics.6b00511 (2016).
10. Shah, R. S., Rey, J. J. & Stewart, A. F. In Laser-Induced Damage in Optical Materials: 2006. 640305 (2007).
11. Cheng, X. et al. Optimal coating solution for a compact resonating cavity working at Brewster angle. *Opt. Express* 24, 24313–24320, https://doi.org/10.1364/oe.24.024313 (2016).
12. Cheng, X. B., Jiao, H. F., Liu, J. T., Ma, B. & Wang, Z. S. Nanosecond pulsed laser damage characteristics of HfO2/StO2 high reflection coatings irradiated from crystal-film interface. *Opt. Express* 21, 14867–14875, https://doi.org/10.1364/oe.21.014867 (2013).
13. Cheng, X. B. et al. Physical insight toward electric field enhancement at nodular defects in optical coatings. *Opt. Express* 23, 8609–8619, https://doi.org/10.1364/oe.23.008609 (2015).
14. Neaport, J. et al. Effect of electric field on laser induced damage threshold of multilayer dielectric gratings. *Opt. Express* 15, 12508–12522 (2007).
15. Cheng, X., Jiao, H., Lu, J., Ma, B. & Wang, Z. Nanosecond pulsed laser damage characteristics of HfO2/StO2 high reflection coatings irradiated from crystal-film interface. *Opt. Express* 21, 14867–14875 (2013).
16. Cheng, X. et al. In SPIE Optical Systems Design. 816816 (International Society for Optics and Photonics).
17. Yan, L. et al. Coupling effect of multi-wavelength lasers in damage performance of beam splitters at 355 nm and 1064 nm. *Appl. Opt.* 51, 3243–3249 (2012).
18. Dumitrache, C., Rath, J. & Yalin, A. P. High Power Spark Delivery System Using Hollow Core Kagome Lattice Fibers. *Materials* 7, 5700–5710, https://doi.org/10.3390/ma7085700 (2014).
19. Humberg, G. et al. Hollow core photonic crystal fibers for beam delivery. *Opt. Express* 12, 1477–1484 (2004).
20. Michaille, L. F. et al. In Integrated Optical Devices, Nanostructures, and Displays. 30–38 (2004).
21. Ye, X. et al. High power laser antireflection subwavelength grating on fused silica by colloidal lithography. *J. Phys. D: Appl. Phys.* 49, 265104 (2016).
22. Florea, C., Sanghera, J., Busse, L., Shaw, B. & Aggarwal, I. In Photonic and Phononic Properties of Engineered Nanostructures. 794610–794618 (2011).
23. Jing, X., Shao, J., Jin, Y. & Fan, Z. Near-field distribution of broadband antireflective nanostructure arrays. *Optik* 123, 527–533 (2012).
24. Hobbs, D. S. & MacLeod, B. D. In Laser-Induced Damage in Optical Materials. 67200L (2007).
25. Li, X., Zou, L., Wu, G. & Shen, J. Laser-induced damage on ordered and amorphous sol-gel silica coatings. *Opt. Mater. Express* 4, 2478–2483, https://doi.org/10.1364/OME.4.002478 (2014).
26. Jonušauskas, L. et al. Optically Clear and Resilient Free-Form µ-Optics 3D-Printed via Ultrfast Laser Lithography. *Materials* 10, 12 (2017).
27. Du, Y. et al. Laser-induced damage properties of antireflective porous glasses. *Opt. Commun.* 285, 5512–5518 (2012).
28. Ye, X. et al. Subwavelength porous silica antireflection coating. *J. Optoelectron. Adv. M.* 13, 532–536 (2011).
29. Zhao, J., Li, Y., Xin, W. & Li, X. Preparation and characterization of three-dimensionally ordered macroporous yttria-stabilized zirconia by aqueous organic gel route. *J. Solid State Chem.* 181, 239–244 (2008).
30. Li, Z. et al. Magnetron sputtering SiC films on nickel photonic crystals with high emissivity for high temperature applications. *Appl. Surf. Sci.* 259, 811–815 (2012).
31. Ling, X., Wang, G., Zhao, Y., Liu, X. & Shao, J. Laser-induced damage of the optical coatings due to organic contamination in vacuum. *Appl. Surf. Sci.* 270, 346–351, https://doi.org/10.1016/j.apsusc.2013.01.028 (2013).
32. Wang, H., Zhang, S., Wang, M. & Ge, X. Preparation of monodisperse polystyrene particles from emulsifier-free miniemulsion polymerization. *Chem. Lett.* 37, 1158–1159 (2008).
33. Pan, L. et al. Synthesis of silica particles with precisely tailored diameter. *Chin. J. Chem. Phys.* 27, 563–567 (2014).

Acknowledgements
We thank National Natural Science Foundation of China (No. 51572058, 51502057), Heilongjiang Postdoctoral Fund (NO. LBH-Z15078, No. LBH-Z16080), China Postdoctoral Science Foundation (No. 2016M601427), Aerospace support fund (NO. JZ20150048), the International Science & Technology Cooperation Program of China (2013DFR10630, 2015DFE52770), National Key Research & Development Program (2016YFB0303903), and the Foundation of Science and Technology on Advanced Composites in Special Environment Laboratory.

Author Contributions
Dr. Pan conducted the simulation and drafted the manuscript. Dr. Xu contributed to the analysis of the results. Miss Lv conducted the LIDT test experiments. Prof. Qiu conceived the simulation. Prof. Zhao conceived the preparation experiments of PS 3DPCs. Prof. Li put forward the whole research plan. All authors reviewed the manuscript.

Additional Information
Competing Interests: The authors declare no competing interests.

Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.