# High-performance laser mode-locker with glass-hosted SWNTs realized by room-temperature aerosol deposition

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**Abstract:** We preserve optical nonlinear properties of single-walled carbon nanotubes (SWNTs) within $SiO_2$-host employing aerosol deposition (AD) that guarantees the formation of dense ceramic thick films at room temperature without combustion and solubility limitation of the SWNTs. The intact nonlinearity is verified with transmittance check, Raman spectrometry and electron microscopes. As a saturable absorption device, the $SiO_2$-SWNT composite film successfully mode-locks fiber lasers inducing high-quality output pulses with the measured pulse duration and repetition rate of 890 fs and 9.52 MHz, respectively. After experiencing the intracavity power higher than 20 dBm, the hosted SWNTs are survived to function as the pulse formers.



**OCIS codes:** (140.7090) Ultrafast lasers; (190.4370) Nonlinear optics, fibers; (140.4050) Mode-locked lasers; (160.6030) Silica.

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## 1. Introduction

With their extremely high optical nonlinearity along with ultrafast photonic operation, single-walled carbon nanotubes (SWNTs) have paved the way for diversified next generation nonlinear photonic devices and systems [1,2]. In particular, SWNT-based fiber mode-locked lasers operating at telecom spectral window have been actively researched resulting in the successful formation of remarkable femtosecond laser pulses [3–5]. So far, the demonstrated pulsation schemes include (i) direct interaction of SWNTs with the propagating light that penetrates the free standing SWNT layers [3], (ii) direct interaction of SWNTs in a polymer host with the penetrating light [4], and (iii) non-blocking interaction of an evanescent field with SWNTs [5]. Quite recently, the scheme (iii) has been demonstrated to overcome the low thermal damage threshold of SWNTs while keeping the identical pulse forming operation in a high-power regime by managing the interaction with a part of the propagating light. However, for more intensified and sophisticated applications of the same SWNT-based nonlinear elements, as the nonlinear operation depends mainly on the peak power of the injected light, it is considered that the direct interaction scheme is still critically attractive. Unlike the free standing SWNTs for the direct interaction, the SWNTs in a host material have significant advantages such as good heat dissipation, high stability, efficient transfer process to any designed substrate, good compatibility with other device fabrication processes [6–8]. Especially a ceramic host material that can be harmonized with the optical fibers is highly desirable. For example, SWNTs can be doped into the core of an optical fiber structure to maximize the nonlinear effect by their "seeing" the peak power of the guided laser beam.

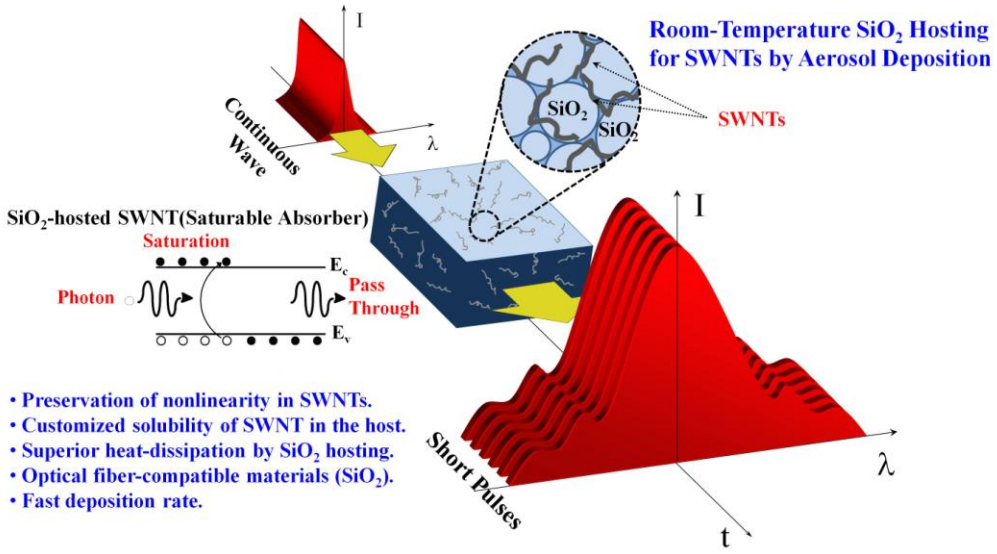


Fig. 1. The schematic of ultrafast pulsation of a fiber laser with the SWNTs embedded into $SiO_2$ host by AD process at room-temperature. The passive mode-locking can be guaranteed by the preserved nonlinearity of SWNTs even within the ceramic host.

Moreover, the ceramic host can provide SWNTs a concrete passivation effect against deleterious oxidation as well as mechanical attacks. So far, unfortunately, only some circumventing approaches have been researched using the hosts of polymer, soft glass, and sol-gel silica since SWNTs cannot be incorporated into the ceramic host at room temperature [4,9,10]. The current problems to be solved also include poor dispersion and solubility of SWNTs in the host material, low reliability, restricted cooling problems from the polymers, and compatibility problems with the silica fibers from the soft glasses [9–13].

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In the present work, we focused on the room-temperature $SiO_2$ hosting for SWNTs employing an aerosol deposition (AD) process [14,15]. Importantly, since the AD process relies on the dried $SiO_2$-SWNT mixture as a starting material, the solubility and the dispersion of SWNTs in the host matrix is not limited. After characterizing its material properties using transmission analysis, Raman spectrometry and electron microscopes, the AD-prepared sample was inserted into a fiber ring laser to realize ultrafast pulse formation by passive mode-locking, which ensured the preservation of the nonlinearity of SWNTs even in the ceramic host as conceptually illustrated in Fig. 1. The pulse quality of the resultant laser was analyzed in both time and frequency domains. The high-power durability of the hosted SWNTs in the direct SWNT-laser interaction scheme was estimated as well.

## 2. $SiO_2$-SWNT composite film prepared on an optical fiber by AD

The operation principle of AD is based on the shock-loading solidification with the impact of ultrafine ceramic particles with the surface of a substrate. Even with the room-temperature and dry deposition condition, the AD-processed ceramic thick films guarantee the superior densification with the theoretical density of over 95% for both mechanical toughness and rapid dissipation of the heat generated from the laser-SWNT interaction. The deposition rate of the AD process can be reached higher than 1 μm/min due to its unique deposition mechanism that can be elucidated by "crush and solidification" of submicron-sized ceramic starting particles [14]. Note that the AD can provide a facilitated tool to fabricate various ceramics-based composite thick films with polymers or metals by designing the composition of the starting powders. Moreover, due to its dry process-mechanism, the AD can be free the solubility limitation of SWNTs that can be found in the solution-based sol-gel process and the polymer-hosting.

The AD apparatus consists of two vacuum chambers that are aerosol and deposition ones connected by a tube. The aerosol chamber has both carrier gas system and vibration system to mix the starting powders with the carrier gas. The aerosol generated in this chamber is delivered to the deposition chamber by the pressure difference between the two chambers. The deposition chamber is for the formation and the patterning of the films. The chamber contains a nozzle, aerosol inlet system, and substrate holder. A rotary vacuum pump coupled to a mechanical booster pump is adopted to ensure the vacuum level of about 100~5000 Pa during the deposition. In order to prepare the designed $SiO_2$-SWNT saturable absorption device by AD process, as starting powders, the mixture of fused $SiO_2$ powders (the average diameter of 200 nm) and SWNTs (synthesized by HiPCo process) were prepared by a ball milling to achieve the uniform dispersion and avoid the deleterious agglomeration that is directly correlated with the nonlinear properties of the SWNTs. The content of the SWNTs in this work was adjusted to 0.1 wt.%. The starting powders were deposited onto a flat facet of an optical fiber ferrule providing the direct interaction of propagating continuous wave (CW) laser with the glass-hosted nanotubes. The distance between the nozzle and the substrate was adjusted to 3 mm, and the substrate was reciprocated to guarantee a uniform deposition on the whole targeted area. Note that the deposition-thickness can be controlled by aerosol density, reciprocating speed, and number of repeat. Figure 2(a) shows the deposited $SiO_2$-SWNT composite thick film on the end facet of an optical fiber ferrule. The deposition speed was 2 mm/sec, and the repeat number was 10. As shown in the scanning electron microscope (SEM) image (see Fig. 2(b)), it was ensured that a dense microstructure of the $SiO_2$-SWNT composite thick film can be achieved by AD with the high deposition rate at room temperature. The dispersed SWNTs surrounded by $SiO_2$ in the composite film can be found in the inset of Fig. 2(b). Even though the high impact energy of the starting powders enabled the dense structure by crushing the $SiO_2$ particles, the morphology of SWNTs were preserved in the film.

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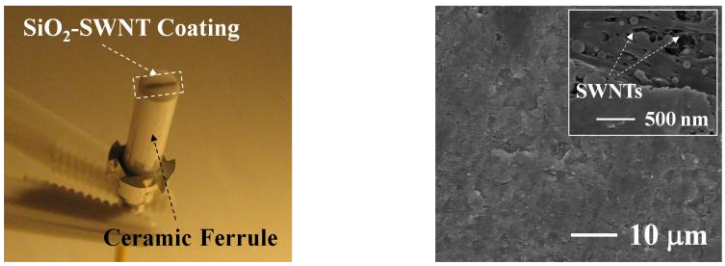


Fig. 2. A deposited $SiO_2$-SWNT composite film on the end facet of an optical fiber by the AD process. (a) A photograph of the deposited film on the ferrule. (b) Scanning electron microscope image of the film. A densified ceramic-SWNT composite formed at room temperature can be seen. Inset shows a zoomed-in structure of the composite identifying the SWNT morphologies in the host.

In order to confirm the existence of SWNTs in the composite film, we analyzed a Raman spectrum of the film deposited on a glass substrate under ambient condition with an argon-ion laser at 514.5 nm, 0.5 mW. As shown in Fig. 3(a), a radial breathing mode (RBM) peak that is an indicating peak corresponding to the coherent vibration of the carbon atoms in the radial direction of the SWNT, G-peak that shows the existence of carbon $sp^2$ network, and D-peak that indicates the degree of perturbation of the carbon network were detected in the $SiO_2$-SWNT composite film. There was negligible peak degradation compared with that of sprayed SWNTs illustrating that SWNTs in the host still keep their morphological characteristics without a significant damage.

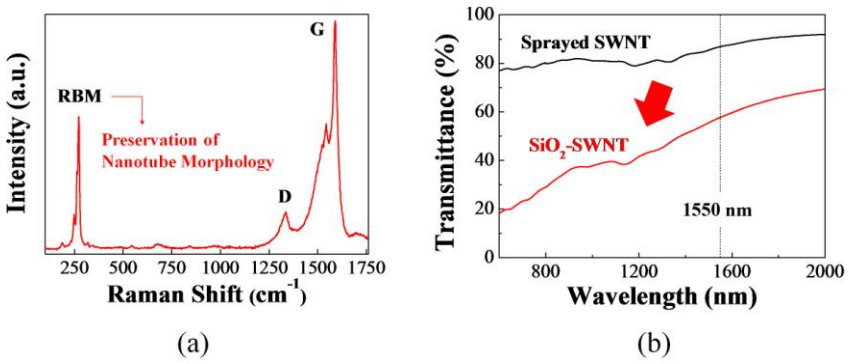


Fig. 3. (a) A Raman spectrum of the deposited $SiO_2$-SWNT composite film on a glass substrate. A characteristic RBM peak of the SWNT was detected in the film. (b) A transmission curve of the composite film describing the preserved nonlinear absorption peak of SWNTs. The curve was compared with that of the sprayed SWNTs.

Figure 3(b) shows the transmission curves of the reference SWNTs sprayed on the glass substrate and the $SiO_2$-SWNT composite thick film on the glass substrate deposited by the AD. In the composite film, the primary $S_1$ absorption peak that is induced by the band-edge transition was found at the center wavelength of about 1250 nm. However, the absorption peak of the glass-hosted SWNTs was slightly shifted to the shorter wavelength direction, and the absorption level got significant as the wavelength decreased. It can be analyzed that the peak shift was from the compressive residual stress in the $SiO_2$ host, and the wavelength-dependent absorption level was originated from the surface contamination of the carbon nanostructures by the surrounded host material as well as the point defects induced during the dynamic deposition process. As a result, we verified that the nonlinear absorption level of the hosted SWNTs can be maintained to ~5% at 1550 nm region.

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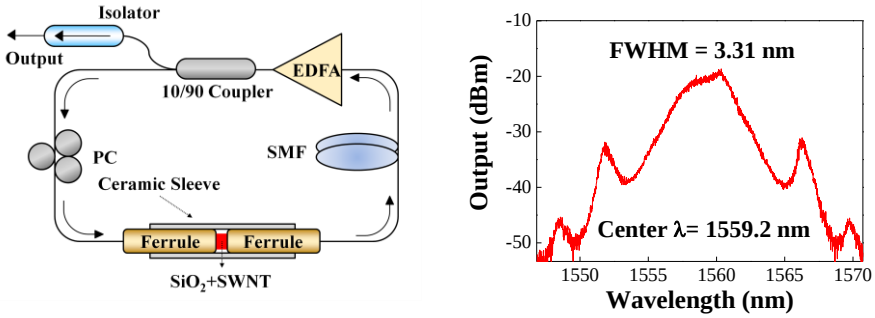
### 3. Passively mode-locked laser functioned by the $SiO_2$-hosted SWNTs

We experimentally verified the preserved nonlinear saturable absorption of SWNTs with being hosted into $SiO_2$ by AD process resulting in high-quality femtosecond pulse formation of fiber lasers with passive mode-locking. The saturable absorber was fabricated by coating the $SiO_2$-SWNT thick film onto an optical fiber ferrule by AD, and inserted into the ring laser cavity by sandwiching the film with additional fiber ferrule and zirconia sleeve providing a beam path through the deposited film. As described in Fig. 4(a), the fiber ring laser setup includes an erbium-doped fiber amplifier (EDFA) that was used as a gain medium, a polarization controller (PC) that matches the roundtrip state of polarization (SOP) in the laser cavity, a 10/90 fiber coupler that yields the resultant pulsed output, an isolator located at the output port that blocks deleterious reflection back from the end facet of the port, and a piece of single mode fiber (SMF) of 1 m that optimizes the intracavity chromatic dispersion distribution. Unidirectional operation of laser is guaranteed by the isolator located at the output port of the EDFA.

As a result, the femtosecond pulses were realized from a single-stage oscillator that incorporating the hosted SWNTs demonstrating the survived carbon nanostructures, therefore intact nonlinearity under the AD process. When the input current into the EDFA was reached to 150 mA and the SOP was adjusted, the mode-locking was started with the output power of 3.02 dBm. Once the mode-locking was achieved, the mode-locking was self-started when we turned off and on the laser. Figure 4(b) shows the optical spectrum measured by an optical spectrum analyzer (OSA) with the resolution level of 0.05 nm. The center wavelength and the spectral full width at half maximum (FWHM) are 1599.2 nm and 3.31 nm, respectively. The extinction ratio read in the OSA spectrum was over 30 dB as can be seen in the figure. The slight continuous wave (CW) component on the spectrum top can be controlled with the re-optimization of cavity condition including power level, polarization state, dispersion level as well as all the intracavity connections. For the stability test of the pulsation operation, we left the laser for hours to find no significant drift of the center wavelength and/or the degradation of the spectrum shape. It can be explained that the noise-like tiny ripples on the spectrum line come from the imperfect connection within the laser cavity, thereby inducing the sub-cavity effects.




(a) (b)

Fig. 4. (a) Fiber ring laser setup and the composite-based mode-locker assembly. (b) The measured optical spectrum from the output port. The center wave length and the 3-dB spectral width are 1599.2 nm and 3.31 nm, respectively.

Figure 5(a) represents the output pulse train formed by the $SiO_2$-hosted SWNTs, and measured with 10 Gbit/s photo-detector. After suppressing the harmonic mode-locking, we achieved the repetition rate of 9.52 MHz that corresponds to the cavity length of 21.0 m, and illustrates that the formed pulses are from the fundamental mode operation. The temporal pulse duration of the individual pulse was measured by an autocorrelator as shown in Fig. 5(b). The measured FWHM was 890 fs when we fitted the data into *sech* curve. As the time-frequency product was 0.363, it can be concluded that the generated pulses have high quality

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but slightly chirped to approach to the transform-limited pulses that has the value of 0.315. Considering the pulse parameters, the pulse energy and the peak power were calculated assuming the *sech* pulse formation to 0.2 nJ and 0.21 kW, respectively, confirming that the fluence level was over μJ/cm$^2$ that is typically required for the saturable absorption of SWNTs [3].

High power operation of our $SiO_2$-SWNT sample was also checked with the intracavity power of 20.8 dBm. Unlike the free standing SWNT that is thermally fragile over the optical power level of 10 dBm in SMF (in case of the direct interaction scheme) [5], the sample still showed the nonlinear intensity modulation after experience the high power injection ensuring the critical role of the ceramic hosting.

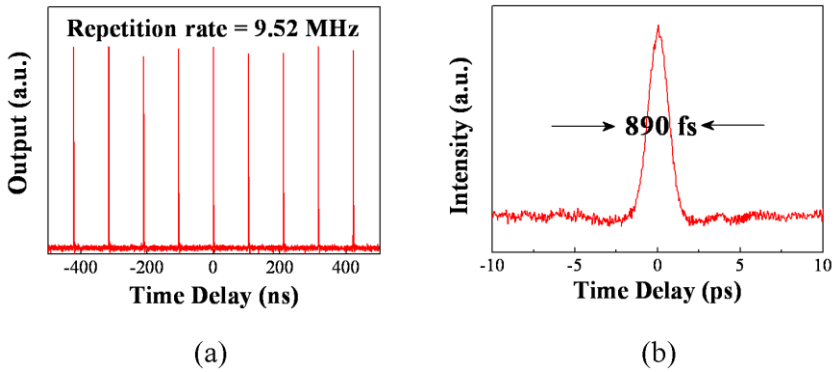


Fig. 5. (a) The output pulse train measured by the oscilloscope. (b) The autocorrelation trace of an individual output pulse ensuring the successful femtosecond pulse formation.

## 4. Conclusion

Targeting for the effective direct interaction of SWNTs and propagating laser light, we demonstrated the hosting SWNTs into a ceramic matrix using the AD process in a dry and room-temperature process condition. We overcame the limitation originated from the nanotube solubility as well as thermal damage using the extremely effective composite-film preparation process. The preserved nonlinearity of SWNTs in the host were verified by demonstrating a fiber pulsed laser mode-locked by $SiO_2$-SWNT composite thick film as a saturable absorber. We believe that the AD-processed SWNT-composite can open a new phase of the research on the SWNT-nonlinear-optics for the nanotech-based integrated and intensified optical components critically required for the future complex and intelligent information technologies.

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