Supporting Information

Composite film with anisotropically enhanced optical nonlinearity for pulse-width tunable fiber laser

Zhijun Ma [a,*], Zhongliang Hu [a], Hang Zhang [b], Jiulin Gan [a], Changsheng Yang [a], Zhichao Luo [c], Tian Qiao [a], Mingying Peng [a], Guoping Dong [a], Zhongmin Yang [a], Frank W. Wise [d] and Jianrong Qiu [a, e, *]

[a] *State Key Laboratory of Luminescent Materials and Devices, Guangdong Provincial Key Laboratory of Fiber Laser Materials and Applied Techniques, School of Materials Science and Engineering, South China University of Technology, Guangzhou, 510640, China*

[b] *National Key Laboratory of Shockwave and Detonation Physics, Institute of Fluid Physics, Chinese Academy of Engineering Physics, Mianyang, Sichuan, 621900, PR, China*

[c] *Laboratory of Nanophotonic Functional Materials and Devices, School of Information and Optoelectronic Science and Engineering, South China Normal University, Guangzhou, Guangdong 510006, China*

[d] *School of Applied and Engineering Physics, Cornell University, Ithaca, NY 14853, USA*

[e] *College of Optical Science and Engineering, State Key Laboratory of Modern Optical Instrumentation, Zhejiang University, Hangzhou 310027, China.*

**Correspondence: Zhijun Ma, zhijma@scut.edu.cn; Jianrong Qiu, qjr@scut.edu.cn*

Section 1. Supplementary figures

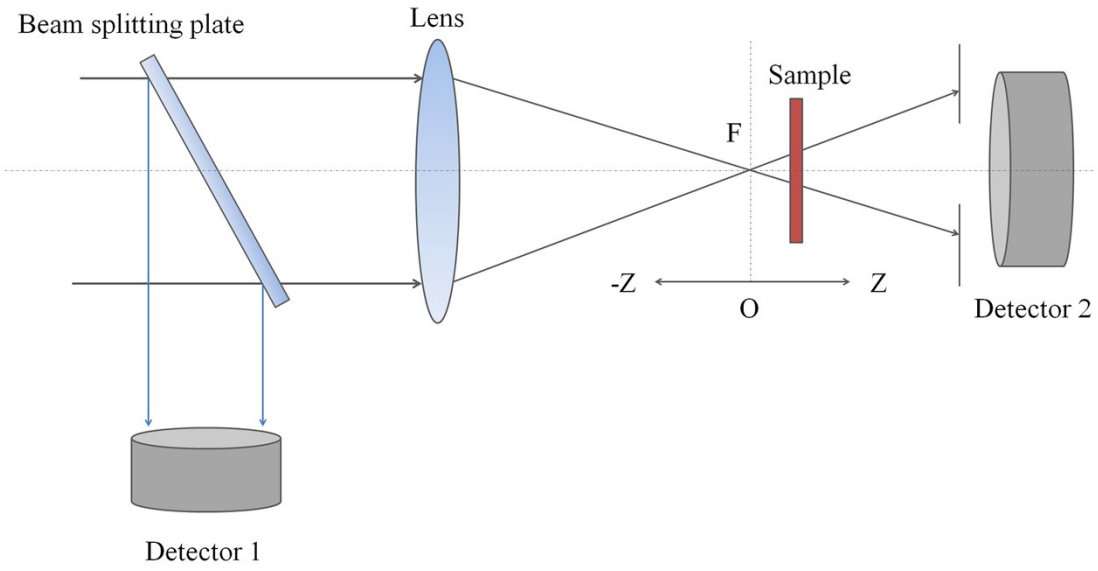

Figure S1-1. A schematic illustration of the Z-Scan setup used for investigation of the nonlinear optical properties in our work.

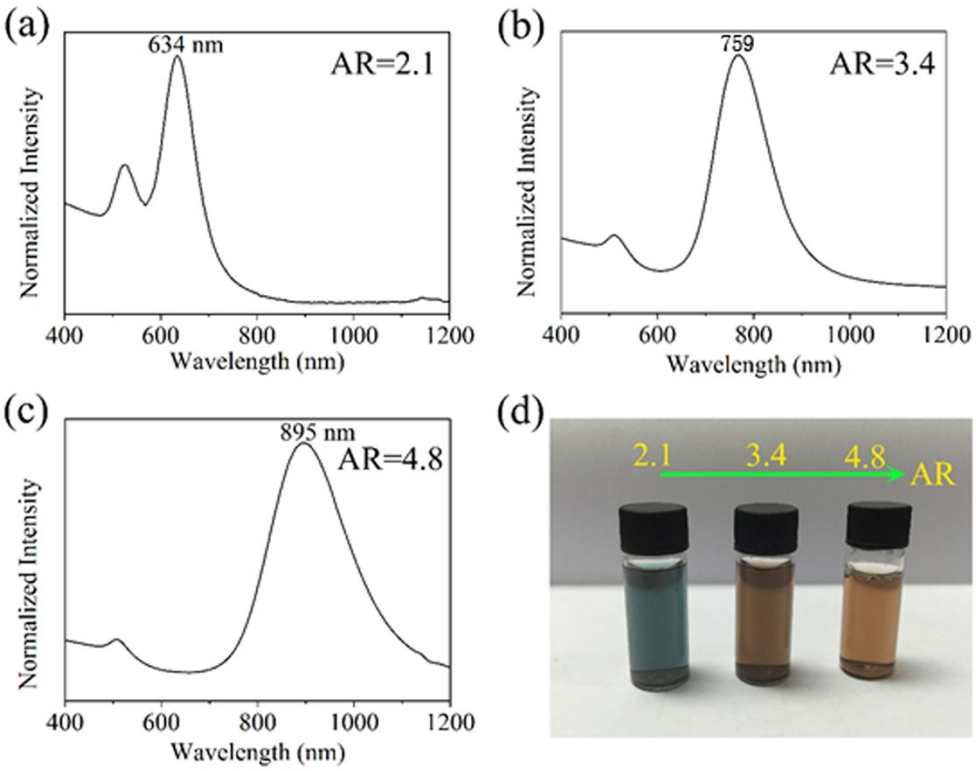

Figure S1-2. | Extinction spectrum of GNRs aqueous dispersion. (a)-(c) normalized extinction spectrum of GNRs. The LSPR peak of GNRs with AR=2.1, 3.4 and 4.8 are 634 nm, 759 nm and 895 nm, respectively, (d) photograph of three different GNRs solution, solution color change from blue to red.

Figure S1-3. | Photograph of the PVA/GNRs-3.4 fibrous film. Length and width of the film are about 300 mm and 70 mm, respectively.

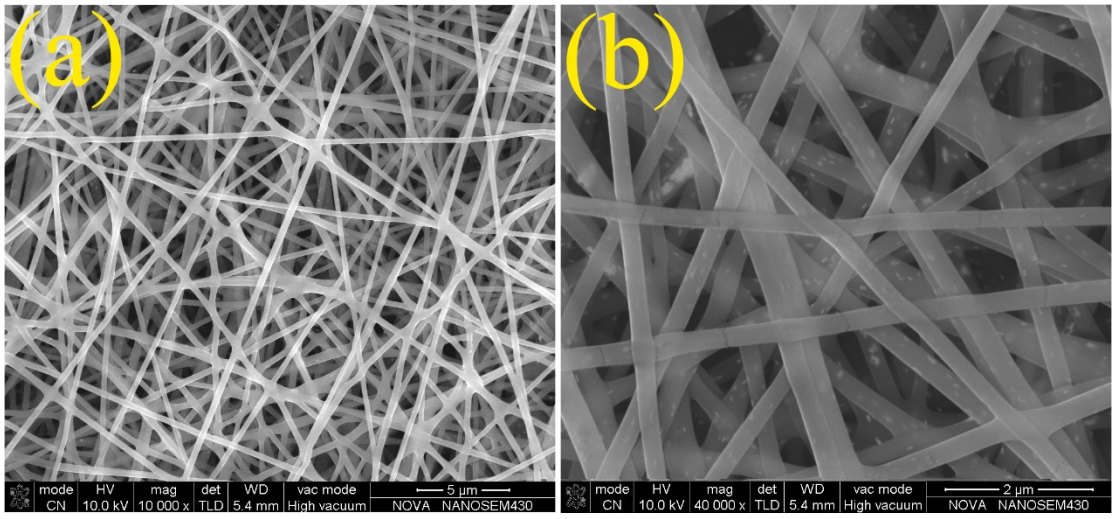

Figure S1-4. | SEM images of Disorder-PVA/GNRs-3.4 film. (a) Magnification of 10000× and (b) 40000×, the white dots in (b) were GNRs.

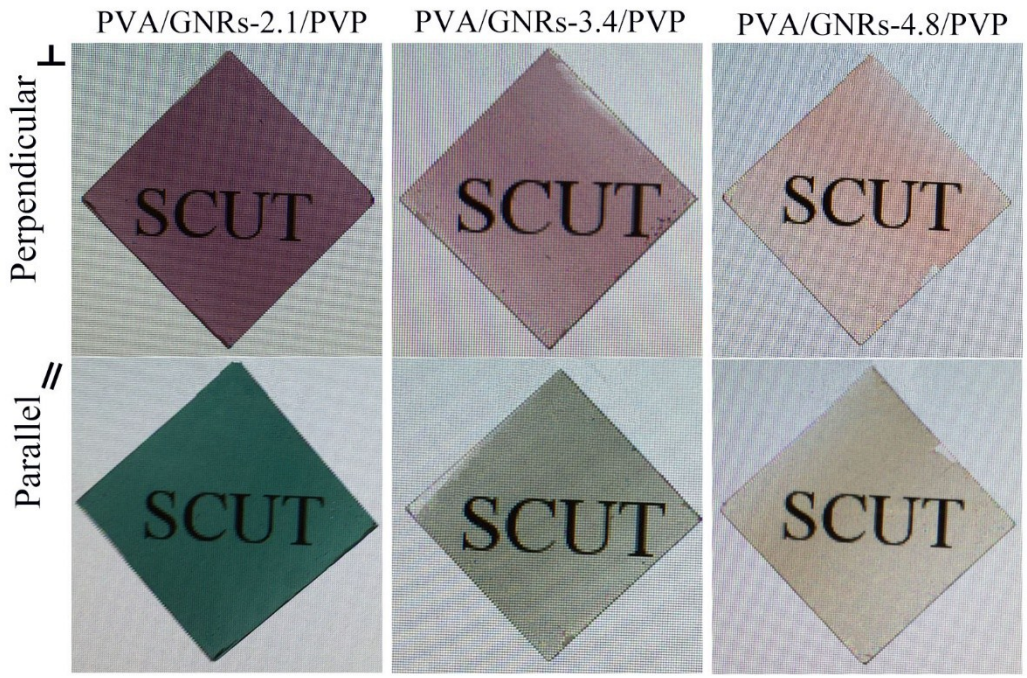

Figure S1-5. | Digital photograph of transparent composite film under white light illumination. Distinct color when the incident light parallel and perpendicular to the long axis of GNRs were observed. The difference is obvious with the LSPR in the visible spectrum.

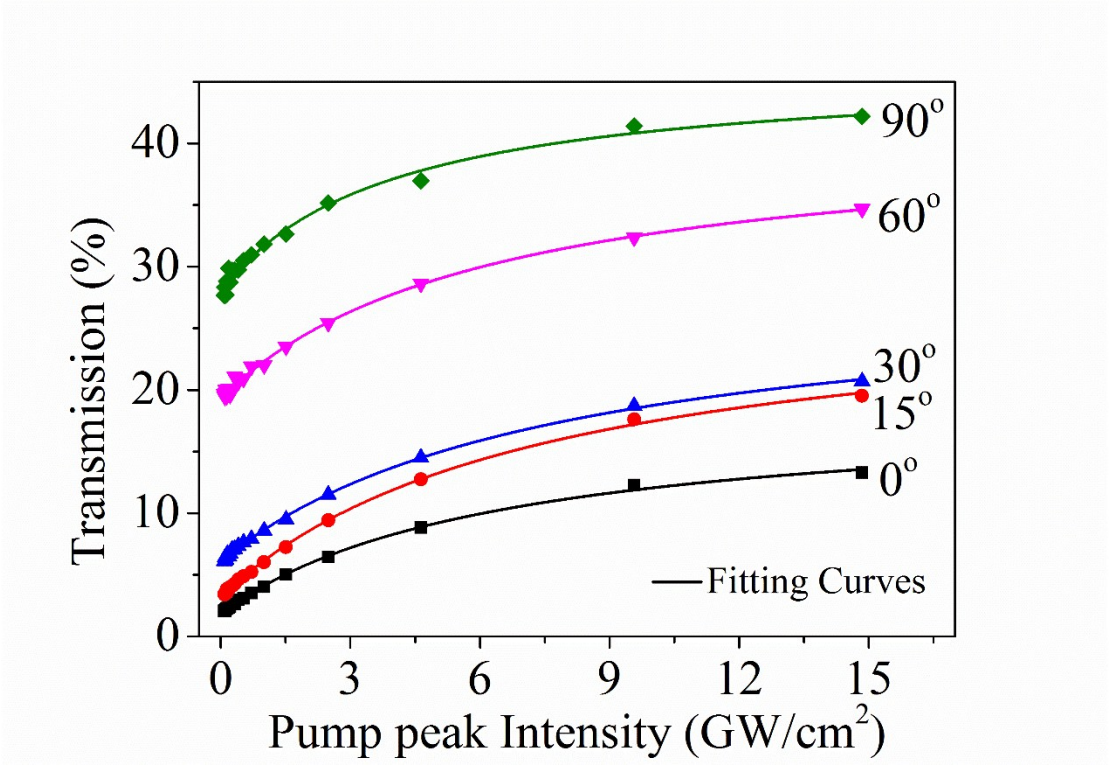

Figure S1-6. | Transmission ration at 800 nm of the PVA/GNRs-3.4/PVP film as a function of the pump power. The experiment data were fitted using equation 2.

Section 2.

2.1 GNRs doping concentration of the composite fiber films

Models of single nanofiber and composite fibrous film

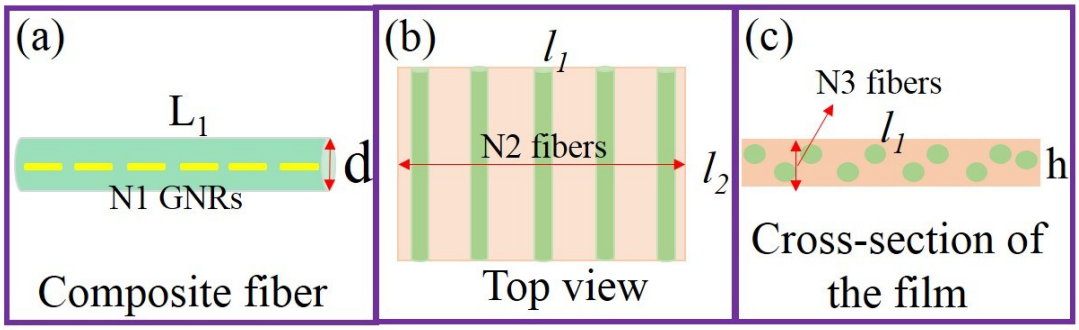

Figure 2-1. (a) single fiber with GNRs aligned alone long axis of the fiber, (b)and (c) top view and cross-section of the film.

(a) The concentration of GNRs in single PVA fiber (defined as C1) can be calculated according to number of Gold nanorods aligned inside the fiber (defined as N1, determined by TEM observation): $C1 = \frac{N_1}{\pi(d/2)^2 L_1}$ (N/μm^3).

From (b) and (c) we can calculate the volume percentage of fibers in the whole composite film, the parameter of which can be determined by the surface and cross-sectional SEM images of the film.

Volume of composite film: $V1 = l_1 l_2 h$

Volume of fibers: $V2 = N2 * N3 * \pi(d/2)^2$

Fiber volume percentage: V2/V1

Concentration of GNRs: C=C1*V2/V1

Here we assumed L_1, l_1, l_2 and h equals to 1 μm, and the corresponding value of other parameters (N1, N2 and N3) that obtained from TEM and SEM images are shown in the table. The final calculated concentration (C) of GNRs in the whole film was also shown in table 1.

Supporting Table 1 Parameter of the samples obtained from SEM and TEM images. (C=N1*N2*N3 if we defined L_1, l_1, l_2 and h = 1μm)

parameter	d (μm)	N1 (N)	N2 (N)	N3 (N)	C (N/μm^3)
PVA/GNRs-2.1/PVP	0.17	3.25	1.11	5.56	20
PVA/GNRs-3.4/PVP	0.27	5.28	1.00	3.03	16

PVA/GNRs-4.8/PVP	0.31	4.48	1.25	3.21	18

2.2 Polarization efficiency of the samples (PVA/GNRs-X/PVP films) to 800 nm light.

The polarization efficiency η of the samples can be calculated using the following formula:

$$\eta = \frac{I_{max} - I_{min}}{I_{max} + I_{min}}$$

Supporting table 2 polarization efficiency of the samples.

samples	PVA/GNRs-2.1/PVP	PVA/GNRs-3.4/PVP	PVA/GNRs-4.8/PVP
Imax	0.5958I_0	0.2768 I_0	0.8151 I_0
Imin	0.1849 I_0	0.0207 I_0	0.5688 I_0
η (%)	53	86	18

2.3 β value of single GNRs

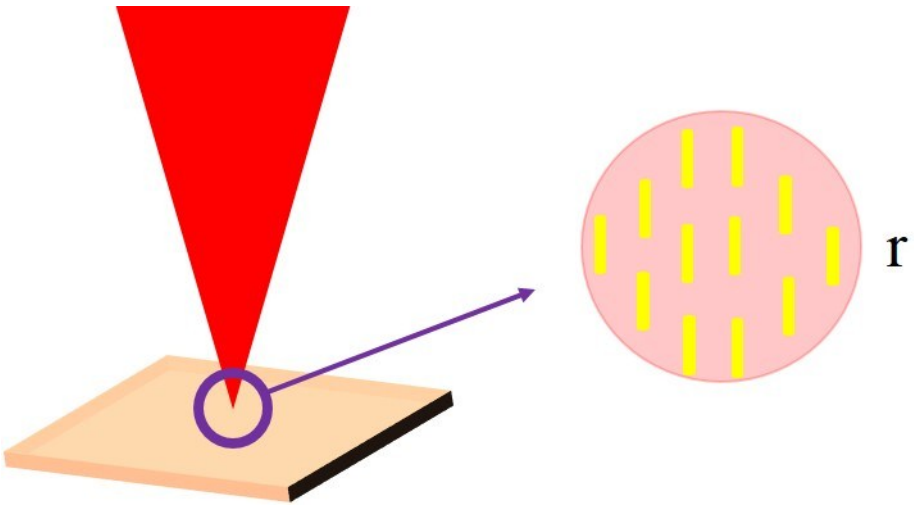

Figure 2-2. 800 nm fs beam focused on the sample.

Radius of fs laser at focus: $r = 1.22\frac{\lambda f}{D}$ where λ is the wavelength (800 nm), f is focal length (150 mm), D is beam diameter (10 mm). The calculated r=15 μm. The film thickness of the three samples are 30 μm, 22 μm, and 22.6 μm, respectively (basically equals to the diameter of the spot size). According to the β value of the film calculated

from Z-scan results, β value of single GNR can be calculated as follows:

$$\beta - single = \frac{\beta}{{}^{4}/_{3}\pi r^{3} C}$$

and the value were shown in supporting table 3.

Supporting Table 3 Calculated β value of single gold Nanorod.

Samples	C (N/μm^3)	β (10^{-8} cm/W)	β-single (10-13 cm/W)
PVA/GNRs-2.1/PVP	20	-6.0	-0.9
PVA/GNRs-3.4/PVP	16	-21.5	-3.6
PVA/GNRs-4.8/PVP	18	-1.4	-0.23