Ultra-broadband Nonlinear Optical Response of Two-dimensional *h*-BN Nanosheets and Their Hybrid Gel Glasses

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S1. Experiment section:

Hexagonal boron nitride was purchased from Alfa Aesar. Sodium hydroxide and potassium hydroxide of analytical reagent grade were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai). Ethanol was purchased from Kermel Reagent Co. Ltd. (Tianjin, P. R. of China). All the reagents were used as received.

In a typical experiment, sodium hydroxide (2.0600 g) and potassium hydroxide (2.7160 g) were ground finely and then h-BN powder (0.2480 g) was added. The mixture was further ground into a homogeneous form and transferred to a poly(tetrafluoroethylene)-lined stainless steel autoclave. The system was heated at 180 ° C for 2 h and then cooled down to room temperature. The autoclave container was taken out and the solid product was collected and dissolved deionized water in a clean vial. And then the vial was capped and bath-sonicated for 24 h. The vial was taken out and a slight odor of ammonia was noticed when the vial was opened. The product was collected and washed with deionized water repeatedly until the pH of the filtrate was close to neutral.

Characterization: To obtain IR spectra, each sample was ground with KBr

powder and the transmittance of each resulting pellet was measured with an FTIR spectrophotometer (Thermo-Nicolet Nexus 670). UV-Vis-near IR spectra were measured on Varian Cary 5000 UV-visible-near infrared absorption spectrophotometer. Scanning Electron Spectroscopy (SEM) was carried out with Hitachi S-4800 field emission scanning electron microscope. Gold powder was sprayed over the fresh sample surface for clearness of image. High-resolution transmission electron microscopy (HRTEM) images were obtained with a Philips Tecnai 20U-Twin high-resolution transmission electron microscope at an acceleration voltage of 200 kV.

OL and NLO effect analysis: The optical limiting properties of the samples were investigated using 8 ns laser pulses from a Nd:YAG laser (Spectra-Physics Quanta-Ray INDI Pulsed Nd:YAG Laser, optical parametric oscillator) at a repetition rate of 10 Hz, and at wavelengths of 532, 1064 and 2000 nm. The pulse energies in front of and behind the sample were monitored by energy detectors D1 and D2 (Ophir Optronics Inc. PE25). The laser beam waist was approximately 7 μm (532 nm), 5 μm (1064) and 7 μm (2000 nm). The solution was contained in 5 mm thick quartz cells, while the solid glass was fixed vertically using a clamp. The linear transmittance (T0) of all samples was adjusted to 75% at 532 nm using a UV-Vis spectrometer. The obtained data were further processed with a computer. For each sample, multigroup experiments were conducted under different energy levels. All measurements were conducted at room temperature.

The third order nonlinear optical properties of BNNSs in ethanol solution and its gel glass were studied using open-aperture and close-aperture Z-scan technique with Nd:YAG laser as light source (the pulse width of 8 ns and wavelength of 532 nm and 1064 nm). The pulse of the Gaussian laser was 8 ns from a Q-switched Nd:YAG laser at a repetition rate of 1 Hz. During the sample propagation along the Z-axis, the transmission energy and nonlinear scattering signal were obtained simultaneously, and were recorded by the detector behind the sample (D1) and the detector at an angular position of 45^{o} relative to the laser direction (D2). BNNSs suspensions were contained in 1 mm thick quartz cells, while the hybrid glasses were wiped clean with

alcohol and then fixed vertically using the specimen holder.

S2. FTIR spectra of samples

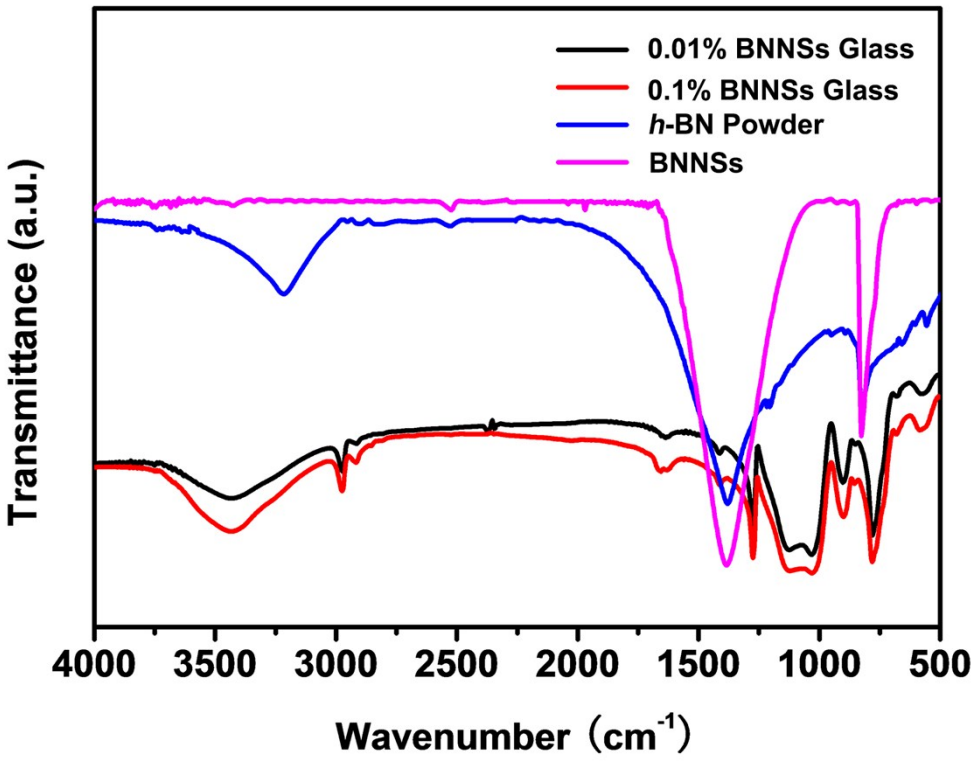

Figure S1. FTIR spectra of h-BN raw materials (blue line)，BNNSs (pink line), 0.01% BNNSs doped glass (black line) and 0.1% BNNSs doped glass (red line), respectively.

S3. Dispersivity of the as-obtained BNNSs

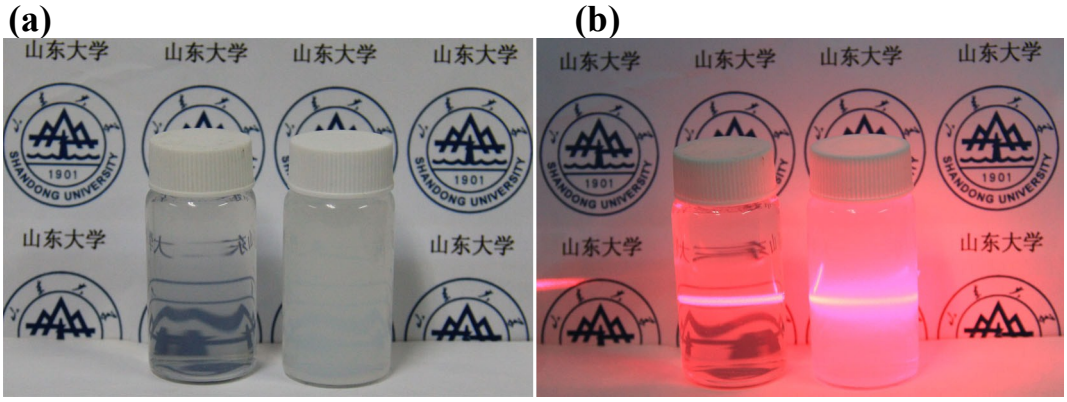

Figure S2. Photograph of BNNSs suspension and their Tyndall effects, the solvents of the dispersion from left to right are ethanol and water. (a) h-BN nanosheets dispersions upon visible light (b) Tyndall effects of the nanosheets dispersions, laser light shone from left.

The dispersivity of our product was revalidated by dispersing the exfoliated h-BN nanosheets in water and ethanol (Figure S2a). When BNNSs dispersions are illuminated using a red laser, the Tyndall effects are observed (Figure S2b). This also proves the good solubility of BNNSs in water and ethanol. The dispersion of our product is very stable, and the dispersion in ethanol has been stable over 30 months. These features make the obtained BNNSs suitable for Ormosil hybrid glasses.

S4. Transmission spectra of gel glasses

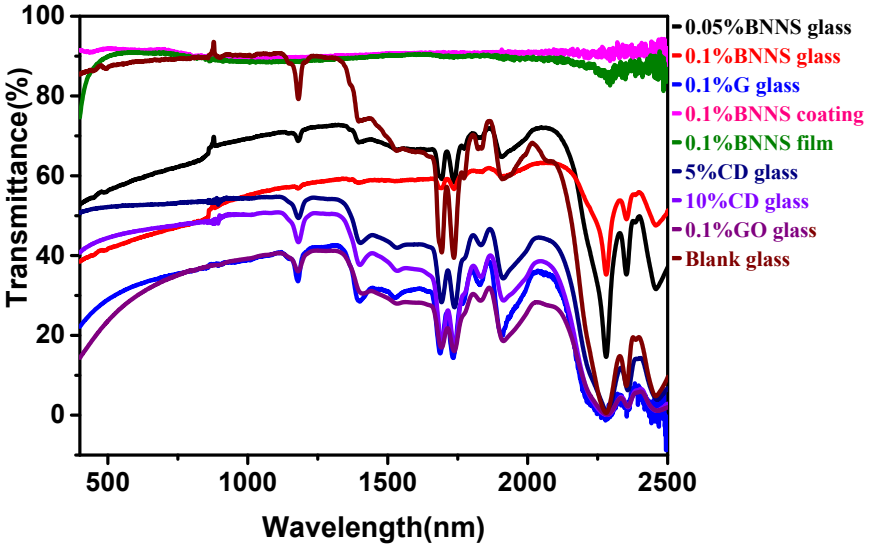

Figure S3. Transmittance spectra of blank and hybrid Ormosil gel glasses solid structures (~0.1 wt%): blank gel glass; 0.05 wt% BNNSs doped glass, 0.1 wt% BNNSs doped glass, 0.1 wt% BNNSs gel coating (on glass) and 0.1 wt% BNNSs self-healing film; 5 wt% and 10 wt% carbon dot (CD) doped gel glass; and 0.1 wt% graphene (G) and 0.1 wt% graphene oxide (GO) doped glass, respectively.