

Highly Dispersed Antimonene Oxide Quantum Dots and Their Hybrid Gel Glasses for Broadband Nonlinear Optical Limiting

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Experimental Section

Materials

Antimony bulk (Sb) was purchased from China new metal materials technology Co., Ltd. Methyltriethoxysilane (MTES) was obtained by Aladdin. Ethanol was obtained from Sinopharm Chemical Reagent Co., Ltd.

Preparation of SbO_x QD

QDs was obtained by the liquid exfoliation method of antimony in isopropanol for 12 h. The sonicated dispersion was centrifuged at 10000 rpm, and the supernatant containing SbO_x QD was carefully collected for further characterization.

Preparation of doping SbO_x QD organically modified silicate gel glasses

MTES was pre-polymerized overnight in ethanol and water (adjusted to pH = 2.5 with acetic acid). Then the volume of the mixture was cut down to half by rotary evaporation. The mixture was kept for an additional week to further polymerize at room temperature. Add SbO_x QD to the mixture and stir, the SbO_x QD /MTES mass ratios in the solutions were set at 0, 0.01 wt%, 0.05 wt%, 0.10 wt%, 0.20 wt% and 2.00 wt% respectively. The solutions were cast into molds at room temperature and the solid samples could be lifted out after two weeks under ambient conditions.

Sample characterization

The structures and morphologies of the samples were examined using transmission electron microscopy (TEM, JEOL JEM-2100F operated at 150 kV). Powder X-ray diffraction (XRD) patterns were collected on a Bruker X-ray diffractometer (D8 focus, Cu K α , $\lambda=0.15178$ nm) with the step of 0.1 s⁻¹. XPS was carried out with ESCALAB 250Xi (Thermo Scientific), using an Al K α X-ray source. The Fourier transform infrared (FTIR) spectra were profiled on an Excalibur HE 3100 (Varian). The UV-vis absorption spectra and transmission spectra were obtained by a Cary 5000 (Varian). The optical limiting properties at 532–1570 nm were obtained by a Nd: YAG laser system (pulse duration of 10 ns and a repetition rate of 10 Hz). The Raman spectra were obtained by a Via-Reflex (Renishaw, England).

Table S1 Concentration of quantum dots in different solvents

Solvents	H ₂ O	EtOH	i-PrOH	DMSO
c (mg/mL)	1.01	1.68	2.75	2.91

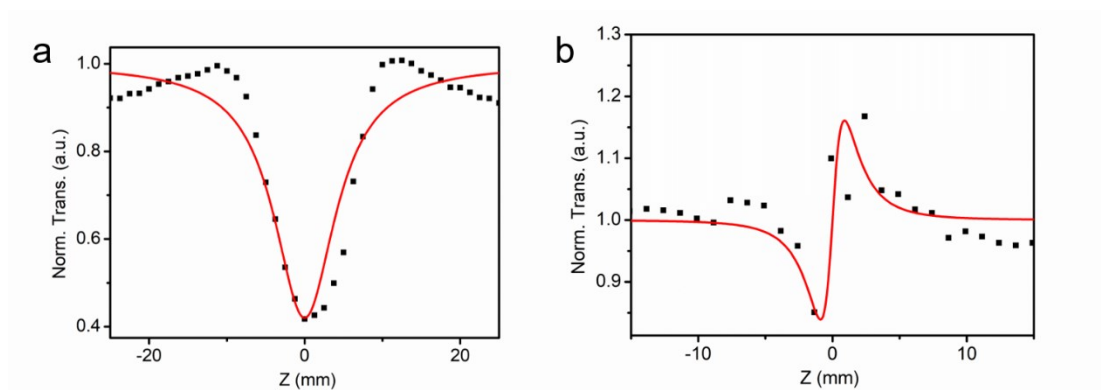


Figure S1 Z-scan results of isopropanol dispersions of SbO_x QD at 1064nm.

- (a) Open-aperture Z-scan nonlinear absorption results;
- (b) closed-aperture Z-scan nonlinear refraction results.

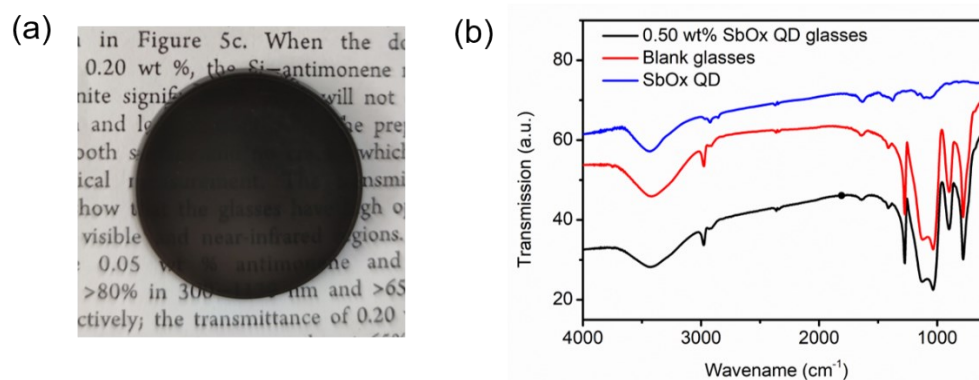


Figure S2 (a) Photographs of gel glasses with 0.50 wt% doping concentrations of SbO_x QD; (b) The FT-IR spectra of SbO_x QD, hybrid glass with SbO_x QD doping concentration of 0.50 wt% and blank MTES glass

In the spectrum of the 0.50 wt% SbO_x QD gel glass. The hydroxyl peak of quantum dots is at 3441 cm⁻¹, the hydroxyl peak of blank glass is at 3417 cm⁻¹, and the hydroxyl peak of gel glass doped with quantum dots is at 3429 cm⁻¹. Compared with blank

glasses, doped with quantum dots are shifted to the higher wave number, broadens the peak, and weakens the peak intensity. All the relatively lower and weaker peaks of 0.50 wt% SbO_x QD glasses was due to hybridization, and this confirmed the hydrogen bonding between the residual silanol groups in the MTES matrix and the hydrogen groups of SbO_x QD.

The glasses were heated to 50, 80, 110, 140 °C for 0.5 h. After the reaction, the glasses were cooled to room temperature for measurement. See the table below. The results are shown in Table S2 and Table S3.

Table S2 The diameter and thickness of blank glass and glass with the doping concentration of 0.2% after heating

Tem (°C)	Blank		0.2% glass	
	Thickness (mm)	Diameter (mm)	Thickness (mm)	Diameter (mm)
30	2.14	29.60	1.83	29.44
50	2.13	29.57	1.83	29.24
80	2.12	29.60	1.80	29.31
110	2.13	29.62	1.82	29.46
140	2.15	29.58	1.84	29.47

Table S3 The photos of blank glass and glass with the doping concentration of 0.2 wt% after heating

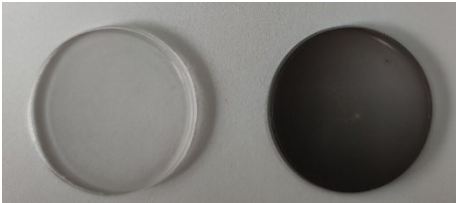


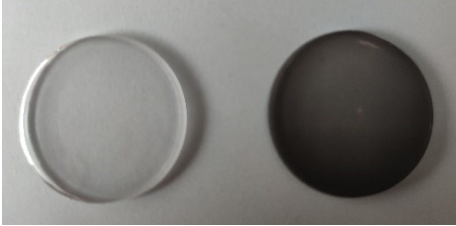
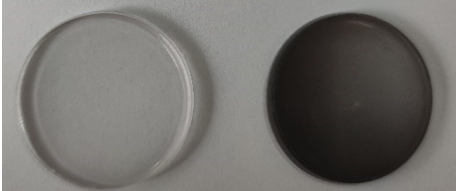
Tem (°C)	Photos (blank at left and 0.2% glass at right)
30	
50	
80	
110	
140	

Table S4 Optical parameters of linear transmittance T_L and NLO onset threshold F_{ON} of the various loading fraction gel glasses at 532, 1064 nm.

Samples	Concentration (%)	532 nm		1064 nm	
		T_L (%)	F_{ON} (J/cm ²)	T_L (%)	F_{ON} (J/cm ²)
1	0.01	88	5.12	91	3.39
2	0.02	86	5.15	91	3.39
3	0.05	72	4.34	84	2.62
4	0.10	63	3.44	76	2.23
5	0.20	40	2.66	62	2.23

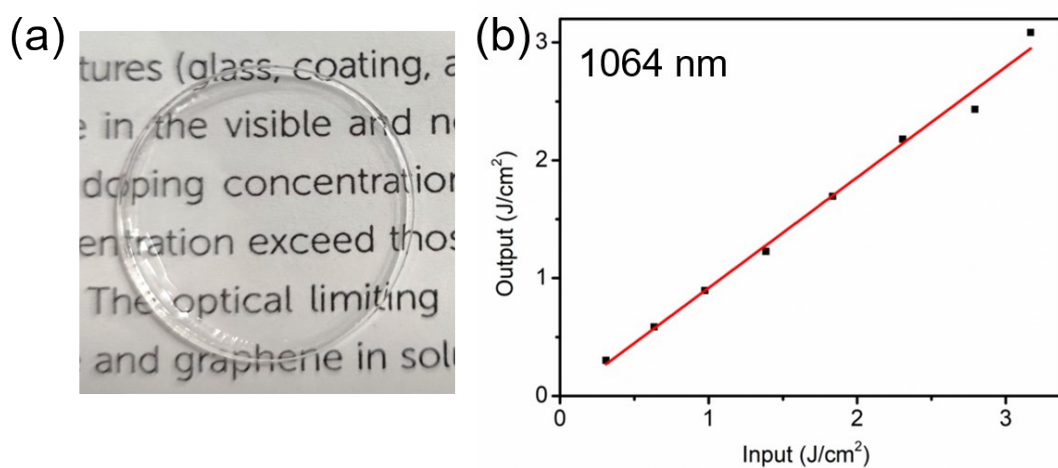


Figure S3 (a) Photograph of blank MTES glass;
 (b) Optical limiting response of blank MTES glass at 1064 nm

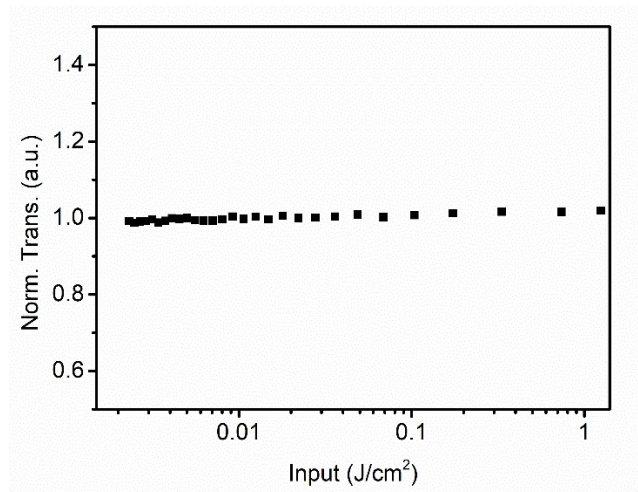


Figure S4 OL curves of isopropanol at 532 nm.

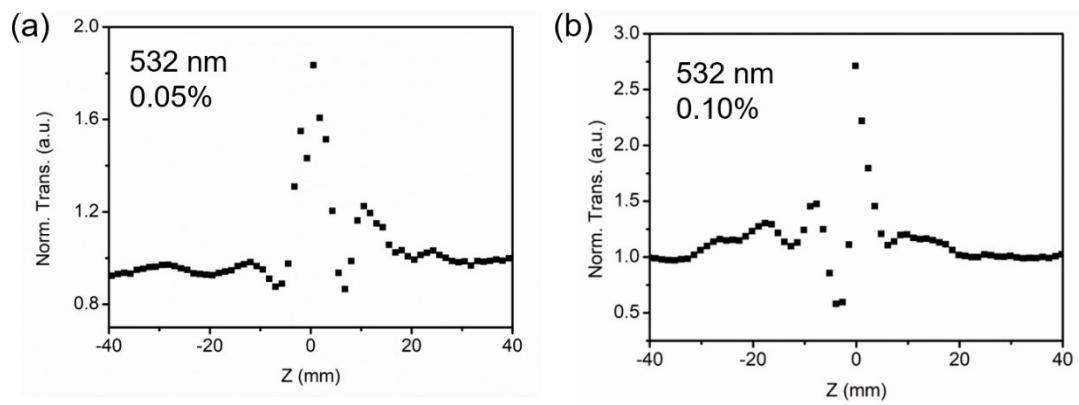


Figure S5 open-aperture Z-scan nonlinear scattering spectra of the hybrid glasses with a doping concentration of 0.05 wt% (a) and 0.10 wt% (b).