

Covalent Functionalization of Sb_2S_3 with Poly(N-vinylcarbazole) for Solid-State Broadband Laser Protection

Guangwei Li^a, Ningning Dong,^{b,d} Xinzhu Wang^{c*}, Xibing Sheng^a, Jun Wang,^{*b,d} Yu Chen^{*a}

^aKey Laboratory for Advanced Materials, Institute of Applied Chemistry, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China. Email: 3148704620@qq.com

^bPhotonic Integrated Circuits Center, Key Laboratory of Materials for High-Power Laser, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, China. Email: jwang@siom.ac.cn

^cChongqing Key Laboratory of Heterogeneous Materials Mechanics, College of Aerospace Engineering, Chongqing University, Chongqing 400040, China.

^dCenter of Materials Science and Optoelectronics, University of Chinese Academy of Sciences, Beijing 100049, China

Experimental Section

General : All reactions were carried out under dry nitrogen atmosphere by using standard Schlenk techniques. Organic solvents were purified, dried and distilled under dry nitrogen. The Sb_2S_3 nanosheets was prepared according to the literature.¹ Ultraviolet/visible (UV/Vis) absorption spectra were measured on a Shimadzu UV-2540 spectrophotometer. The TEM images were recorded on a JEOL JEM-2100 instrument. TGA was carried out on a Perkin–Elmer Pyris 1 thermogravimetric analyzer with a N_2 flow rate of 40 mL min^{-1} at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$. A HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer was used to record the steady-state fluorescence spectra. All samples for the fluorescence measurement were dissolved in water and/or dry organic solvent, filtered, transferred to a long quartz cell, and then capped and bubbled with dry nitrogen for 15 min. Raman spectra were recorded on an Invia/Reflrx Laser Micro-Raman spectrometer (Renishaw, England) with excitation laser beam wavelength of 532 nm.

The NLO and OL performances of the materials were investigated through a standard open-aperture Z-scan apparatus with 6 ns pulses from a Q-switched Nd:YAG

laser at 1064 nm and its second harmonic at 532 nm. The laser beam was focused with a 15 cm lens. For the PMMA-based films, the repetition rate was set to 2 Hz.

Sb₂S₃ functionalized with mercaptoethanol (Sb₂S₃-ME). Sb₂S₃ nanosheets (100 mg) were added into 50 mL of DMF, and then were bath-sonicated for 40 min to give a well-dispersed solution. To the above solution was added 5 mL of mercaptoethanol under stirring, followed by heating at 130 °C for 24 h in the dark under nitrogen atmosphere. After removing the residual mercaptoethanol by vacuum distillation, the obtained Sb₂S₃-ME was re-dispersed into 40 mL of DMF.

Preparation of Sb₂S₃-DDAT as the RAFT agent. To the solution of Sb₂S₃-ME (40 mL) in DMF was added a mixture of DDAT (9.1 g) and *N,N'*-dimethylaminopyridine (DMAP, 1.84 g). After stirring at 0 °C for 1h, 1,3-dicyclohexylcarbodiimide (DCC, 5.19 g) was added to the above solution, followed by reaction for an additional 48h at room temperature. Then the reaction mixture was poured into 300 mL of methanol and vacuum-filtered through a polycarbonate film (φ0.22 μm). The collected product was washed with ethanol, deionized water and THF, respectively, to remove any adsorbed unreacted DDAT. 128 mg of Sb₂S₃-DDAT after dryness under vacuum at 40°C for 24h was obtained.

Preparation of PVK-Sb₂S₃ via RAFT polymerization. Polymerization reaction was carried out under highly purified dry nitrogen by use of standard Schlenk tube. A degassed mixture of Sb₂S₃-DDAT (100 mg) as RAFT agent, *N*-vinylcarbazole (NVC, 200 mg, before use, it was recrystallized twice from methanol at 40 °C, freeze-dried, and stored in vacuum in the dark), AIBN (4 mg) as initiator was heated in a water bath of 75 °C in a ultrasonic generator for 4 h under ultrasonic irradiation. After completion of the reaction, the mixture was allowed to cool to room temperature. The crude product was dissolved in DMF and dropped into 80 mL of methanol, followed by a vacuum-filtering through a polycarbonate film (φ0.22 μm). The collected solid product was washed with a large amount of CH₂Cl₂ to remove any possible unreacted monomer and soluble free PVK polymer (if any) trapped in the resultant product. The product was further purified by Soxhlet extraction with acetone. After drying in vacuum at 50 °C for 6 hours, 184 mg of PVK-Sb₂S₃ powder was obtained.

Preparation of PVK via RAFT polymerization

Polymerization reaction was carried out under highly purified dry nitrogen by the use of a standard Schlenk tube. A degassed mixture of DDAT (10 mg) as the RAFT agent, N-vinylcarazole (200 mg), and AIBN (3 mg) as the initiator was heated in a water bath of 75 °C in a ultrasonic generator for 4 h under ultrasonic irradiation. After completion of the reaction, the mixture was allowed to cool to room temperature. The crude product was dissolved in CH₂Cl₂ and dropped into 120 mL of methanol. This process repeated for at least three times to remove any possible unreacted monomer and initiator. After drying in a vacuum at 50 °C for 6 hours, 191mg of PVK powder was obtained.

Preparation of PMMA-based films : The sample (Sb₂S₃ nanosheets, Sb₂S₃-PVK, the Sb₂S₃:PVK blends) was added to a cyclohexanone solution of PMMA (100 g.L⁻¹) at a partial concentration ~0.5 g.L⁻¹ for Sb₂S₃-PVK, and ~ 1g.L⁻¹ for both the Sb₂S₃ nanosheets and Sb₂S₃:PVK blends with a weight ratio of 1:1. This was followed by sonic agitation until a well-dispersed solution was formed. By using multilayer conventional spin casting technique, we achieved PMMA-based films which were further dried at 60°C for 24 h under high vacuum to remove any possible residual organic solvent before NLO measurements.

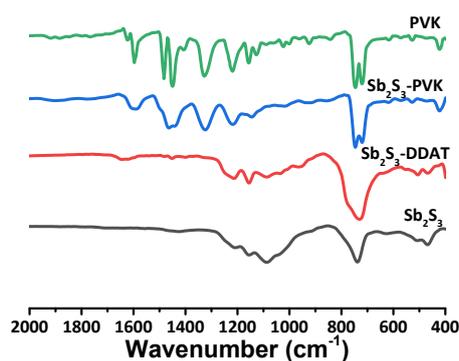


Figure S1. FTIR spectra of the samples.

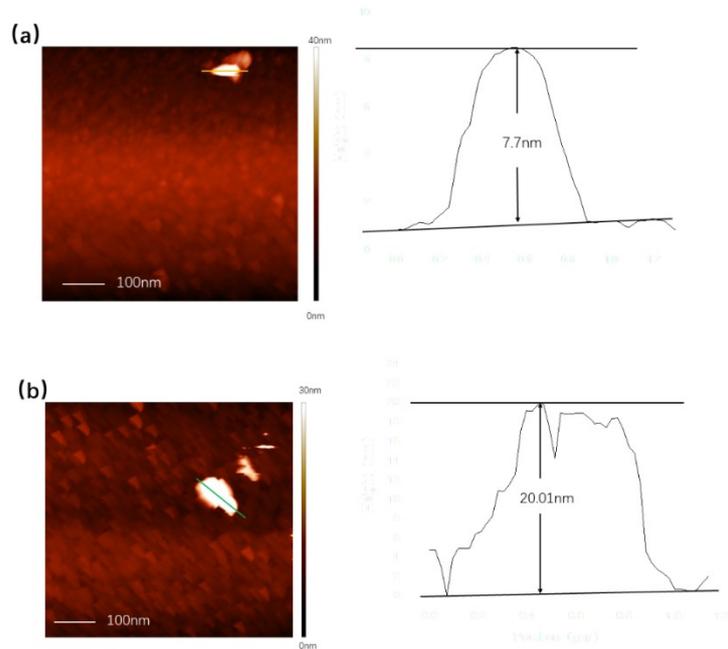


Figure S2.

AFM images of (a) few-layer Sb_2S_3 nanosheets and (b) Sb_2S_3 -PVK.

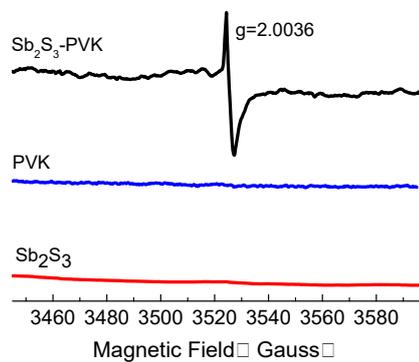


Figure S3. EPR spectra of the samples.

Table S1. Linear and NLO data of the samples. E_1 : input pulse energy; T_0 : linear transmittance; α_0 : linear absorption coefficient; β_{eff} : nonlinear coefficient; $\text{Im}\chi^{(3)}$: imaginary third-order susceptibility.

Laser	E_1	PMMA-based Films	T_0 (%)	α_0 (cm^{-1})	β_{eff} (cm/GW)	$\text{Im}\chi^{(3)}$ ($\times 10^{-12}$, esu)
532 nm 2 Hz	300 μJ	Sb_2S_3	63.31	48.85	98.97	42.26
		Sb_2S_3 :PVK blends	76.75	28.63	110.30	47.09
		Sb_2S_3 -PVK	69.95	33.68	411.79	175.83
		Annealed Sb_2S_3 -PVK	72.04	40.31	478.037	204.12
1064 nm 2 Hz	500 μJ	Sb_2S_3	63.31	48.85	-15.94	-13.62
		Sb_2S_3 :PVK blends	76.75	28.63	107.37	91.80
		Sb_2S_3 -PVK	69.95	33.68	242.79	207.58
		Annealed Sb_2S_3 -PVK	72.04	40.31	520.921	445.39

References

- [1] C. Wu, C. Zhao, L. Wang, Z. Xie, Z. Wang, S. Zhou, *ACS Appl. Nano Mater.* **2021**, *4*, 13425-13431.