

Supporting Information for

Cu-Sn-S plasmonic semiconductor nanocrystals for ultrafast photonics

Qiangbing Guo,^a Meixi Ji,^a Yunhua Yao,^b Meng Liu,^c Zhi-Chao Luo,^c Shian Zhang,^b

Xiaofeng Liu ^{*a} and Jianrong Qiu ^{*d}

^aState Key Laboratory of Modern Optical Instrumentation, School of Materials Science & Engineering, Zhejiang University, Hangzhou 310027, China.

^bState Key Laboratory of Precision Spectroscopy, East China Normal University, Shanghai 200062, China.

^cGuangdong Provincial Key Laboratory of Nanophotonic Functional Materials and Devices, School of Information and Optoelectronic Science and Engineering, South China Normal University, Guangzhou, Guangdong 510006, China.

^dState Key Laboratory of Modern Optical Instrumentation, College of Optical Science and Engineering, Zhejiang University, Hangzhou 310027, China.

Materials and methods

Chemicals.

Copper(I) chloride (CuCl, anhydrous, 99.99%), Tin (II) acetate (Sn(ac)₂, 99.9%), sulfur powder (S, 99.99%), oleic acid (OA, 90%), oleylamine (OAm, 98%), 1-dodecanethiol (DDT, 98%) were purchased from Alfa Aesar. Ethanol (anhydrous, 99.9%), chloroform (anhydrous, 99.95%) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received without further purification.

Synthesis of CTS nanocrystals.

In a typical synthesis, using common air-free Schlenk line techniques, copper and sulphur precursor solutions were formed in two separate round bottom flasks, respectively. In the first flask, the OA-S precursor was prepared by heating 1 mmol of S powder in 10 ml OA to 110 °C under nitrogen protection, and held at this temperature for 20 min followed by heating to 150 °C for another 15 min. Then the OA-S precursor was cooled down to room temperature for the following use. In the other flask, a total of 1 mmol of CuCl and Sn(Ac)₂ powder at a specified ratio were mixed with 20 ml OAm and heated to 110 °C under nitrogen protection to degas for 30 min, then the solution was heated to 210 °C and became transparent. After the temperature had been decreased to 150 °C, 10 ml of OA-S precursor was rapidly injected and the mixture was held at this temperature for 20 min, then the heating mantle was removed and 20 ml ethanol was injected, reducing the temperature to ~ 50 °C. The nanocrystals were collected by centrifugation at 9000 rpm for 3 min, followed by washing 2-3 times by precipitating in ethanol and redissolving in

chloroform. Finally the collected nanocrystals were dispersed in chloroform for further use.

Characterizations of synthesized nanocrystals

Transmission electron microscopy (TEM) images were taken on a JEOL JEM-2100F microscope equipped with a field-emission gun working at 200 kV. Powder X-ray diffraction (XRD) was recorded on RIGAKU D/MAX 2550/PC with Cu K α X-rays. UV-vis-NIR spectroscopy was performed on a Hitachi 4100 UV-vis-NIR scanning spectrophotometer.

Z-scan measurement

The nonlinear optical properties of the plasmonic nanocrystals were investigated with open aperture Z-scan technique. A pulsed laser with repetition rate of 1 kHz and 50 fs pulse duration at wavelength of 1550 nm was used, which was produced by an optical parametric amplifier (OPA, TOPAS-PRIME) pumped by a Ti: Sapphire femtosecond laser (spectra-physics, 800 nm, 1 kHz, 700 mW). The sample (prepared by casting the nanocrystals solution on a 0.5 mm thick high-purity quartz slide) was exposed to different optical intensities by translating it along the optical axis of the focused laser beam and the change of transmitted light was measured as function of the optical intensity.

Pump-probe test

The transient dynamic response was measured with a femtosecond laser (spectra-physics, 800 nm, 500 Hz, 700 mW) equipped with an OPA (TOPAS-PRIME). The transmittance of a weak probe as a function of delay between the probe and a

strong pump of the same wavelength was recorded. It has been examined that the pump beam could not cause any damage to the sample and the probe beam alone could not cause any nonlinear effect in our experiment.

Mode-locking experiment

The schematic illustration of ultrafast fiber laser based on the plasmonic nanocrystals deposited microfiber as SA was shown in Fig. 5. A ~ 7.29 m Er-doped fiber (EDF) (gain medium), along with other 33.66 m standard single mode fiber (SMF), was used with the fundamental repetition rate to be 4.99 MHz. A polarization-independent isolator (PI-ISO) was employed to ensure unidirectional light propagation as well as two polarization controllers (PCs) to adjust the polarization state of the propagation light. Taken by a 10% fiber coupler, the laser output was simultaneously measured by an optical spectrum analyzer (OSA, Yokogawa AQ6317C) and a high-speed real-time oscilloscope (Tektronix DSA-70804, 8GHz) with a photodetector (Newport 818-BB-35F, 12.5 GHz). In addition, the corresponding pulse profile was identified with an autocorrelator (FR-103XL).

Supplementary data

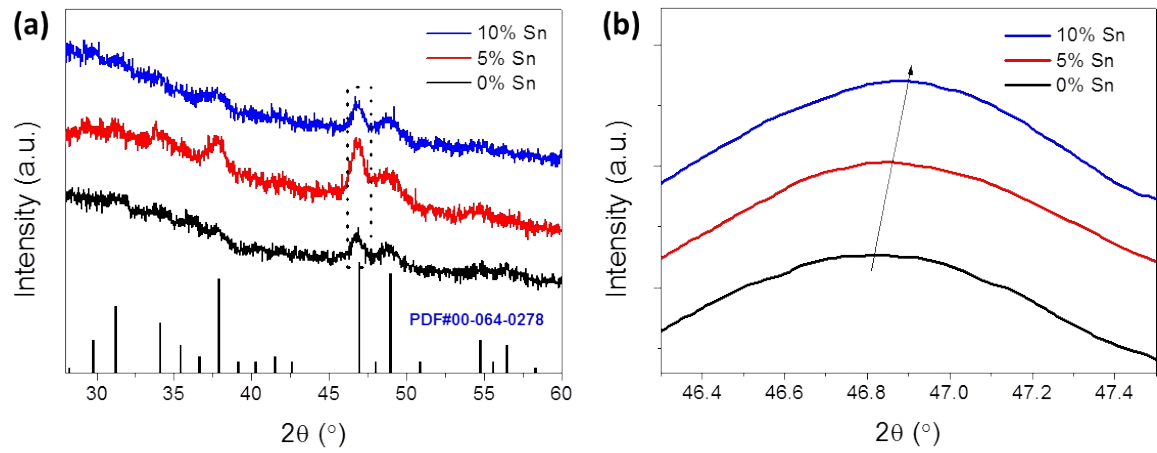


Fig. S1 (a) X-ray diffraction pattern of the synthesized nanocrystals. (b) Enlargement of the indicated part in (a), which shows a gradual increase of the diffraction peak with doping content of Sn as a result of the shrink of the lattice induced by Sn doping.

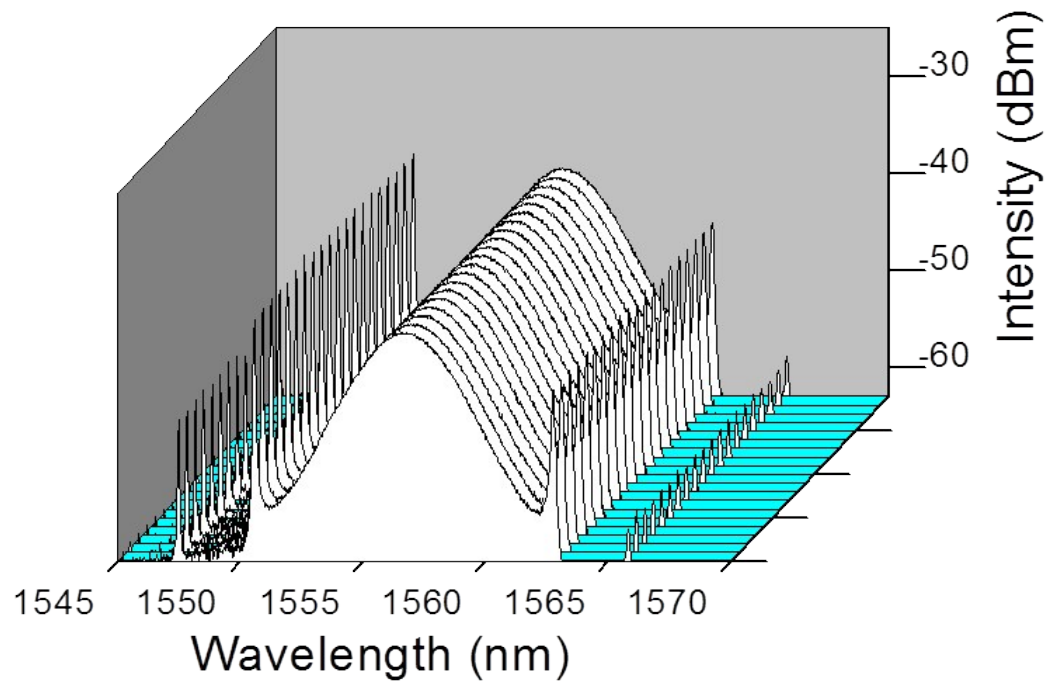


Fig. S2 Repeatedly recorded mode-locked spectrum twice each hour at regular intervals. It is noteworthy that the central wavelength and mode-locked spectral bandwidth are reasonably stable over the time period, indicating a robust performance of the plasmonic semiconductor nanocrystals based saturable absorber against photon damage.

Table 1 Nonlinear optical parameters of several SA materials

Materials	laser	β (cm/GW)	$Im\chi^{(3)}$ (esu)	FOM (esu cm)
SWNTs ¹	1550 nm, 150 fs	N/A	10^{-10}	N/A
Graphene ²	790 nm, 80 fs	$-(2-9)\times 10^{-8}$	$\sim 10^{-12}$	$(3-5)\times 10^{-15}$
MoS ₂ ³	800 nm, 100 fs	-4.6×10^{-3}	-2.52×10^{-15}	1.06×10^{-15}
Black phosphorus ⁴	1550 nm, 35 fs	-0.15×10^{-3}	N/A	N/A
Au nanorods ⁵	800 nm, 220 fs	-1.5	-1.2×10^{-12}	3×10^{-14}
Cu-Sn-S NCs ^a	1550 nm, 50 fs	-134	-1.16×10^{-10}	6.28×10^{-15}

^aThis work

References

1. Chen Y.-C. *et al. Appl. Phys. Lett.* **81**, 975-977 (2002).
2. Kumar S. *et al. Appl. Phys. Lett.* **95**, 191911 (2009).
3. Wang K. *et al. ACS Nano* **7**, 9260-9267 (2013).
4. Wang Y. *et al. Appl. Phys. Lett.* **107**, 091905 (2015).
5. Elim H.I., Yang J., Lee J.-Y., Mi J. & Ji W. *Appl. Phys. Lett.* **88**, 083107 (2006).