

Supporting Information

Quantum-sized silicon for enhanced photoluminescence and optical nonlinearity

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Experimental Section

Materials: Silicon (Si, powder, 10 μ m, 99.9%), Tetraethyl orthosilicate (TEOS), N-methyl-2-pyrrolidone (NMP) and dimethylformamide (DMF) were purchased from Shanghai Macklin Biochemical Co., Ltd. Sodium citrate, N-[3-(trimethoxysilyl)propyl] ethylenediamine (DAMO) were purchased from Aladdin Industrial Corporation. Tetrahydrofuran (THF), acetone, isopropanol (IPA), ethanol, and aqueous ammonia (25.0-28.0%) were purchased from Beijing Chemical Works. All of the materials were used as received. Deionized water was used in the experiments.

Synthesis of silica microspheres: Silica microspheres (SiO₂) were synthesized by the Stöber process.¹ Detailed synthesis could be found in our previous reports.^{2,3}

Production of SiNPs with varying sizes: 10 μ m Si bulk powder (0.7 g), 450 nm silica microspheres (7 g) and 3 mm agate balls (70 g) were mixed and put into an agate jar (under argon atmosphere) for ball-milling (Planetary ball mill, ZQM-2L Changsha Mitr Instrument Equipment Co., Ltd) at 400 rpm for controlled times (i.e., 3, 6, 9, 12, 18, and 24 h). The powder mixture was separated from the agate balls by the screen mesh (pore size 1 mm). The as-separated mixture was dispersed in NMP with concentration of approximately 55 mg mL⁻¹ (i.e., 5 mg mL⁻¹ for the Si bulk powder concentration) for sonication (Vibra-Cell Ultrasonic Liquid Processor, VCX800, SONICS) at 160 W for 5 h. Then, the dispersions were centrifuged at 1500 rpm for 2 hours to remove silica microspheres. The upper 2/3 liquids were collected as the stock dispersions for liquid cascade centrifugation. The centrifugation rate was stepwise increased from 2 to 16 krpm with fixed interval of 2 krpm. After each centrifugation (30 min), the precipitate (Si nanoparticles, SiNPs) was collected. The quantum dots (QDs) in the dispersions after the centrifugation at 16 krpm were collected by solvent precipitation and centrifugation separation. In brief, by adding the poor solvent (hexane) and cosolvent (IPA) into the dispersion with optimized volume ratio (dispersion/poor solvent/cosolvent = 5/10/2), the SiQDs in the dispersions after the

centrifugation at 16 krpm were efficiently precipitated. The following centrifugation (6000 rpm, 30 min) enabled the rapid collection of the QD precipitates. The SiNP dry powders were obtained by vacuum drying. The production yield was calculated by the weight ratio between the NP powder and the bulk powder. Note that a blank (control) experiment was carried out for direct comparison. Similar to the above process, silicon particles were obtained by simple ball milling (without silica microspheres) at 400 rpm for 24 h.

Production of SiNPs through solution synthesis: The colloidal SiNPs were synthesized through a one-pot hydrothermal method. Detailed synthesis could be found in previous reports.^{4,5}

Fabrication of SiNPs-PMMA thin films: The SiNPs-PMMA hybrid thin films were fabricated through solution processing. In brief, PMMA was dissolved in NMP to form a 400 mg mL⁻¹ solution by magnetic stirring overnight at increased temperature. Meanwhile, the SiNPs with varying sizes were dispersed in NMP to form 1 mg mL⁻¹ dispersions by sonication. Based on the pre-designed loading contents and the as-required constant total weight, the PMMA solution and SiNPs dispersion was mixed by vigorous stirring and sonication. The mixture with known volume was dropped into a PTFE mold (a 8µm thick polyimide film as the releasing layer). After complete removal of the solvent from the evenly spreading mixture by moderate heating (70 °C) overnight on a hot plate, the SiNPs-PMMA thin films were obtained.

Characterization: Scanning electron microscopy (SEM) images were acquired using a Hitachi SU8220 microscope. Transmission electron microscopy (TEM) images and high-resolution TEM (HRTEM) images were acquired using an FEI Tecnai F20 U-TWIN microscope operated at 200 kV. Atomic force microscopy (AFM) images were acquired using a Bruker MultiMode 8 AFM using SCANASYST-AIR cantilevers with a nominal tip radius of 2 nm in a scanasyst mode. X-ray diffraction (XRD) patterns were recorded using D/Max-TTRIII (CBO) with Cu Ka radiation ($\lambda=1.54056 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) measurements were

conducted using an ESCALAB 250Xi electron spectrometer from VG Scientific with 300 W Al K α radiation. Small-angle X-ray scattering (SAXS) measurements were performed at the Xeuss WAXS/SAXS system ($\lambda = 1.54 \text{ \AA}$). Scattered X-rays were detected by using a Dectris Pilatus R 300K photon counting detector. Ultraviolet-visible (UV-vis) absorption spectra were recorded using a Lambda 950 spectrophotometer from PerkinElmer. Raman spectra were recorded using a Renishaw inVia plus spectrometer with a 514 nm laser. Photoluminescence (PL) measurements were conducted using a HORIBA FluoroMax+ spectrofluorometer with varying excitation wavelengths. Nonlinear absorption measurements were performed with 100 fs pulses from a Coherent Astrella regenerative amplifier. The laser was operated at 800 nm wavelength with a pulse repetition rate of 1 kHz. All photographs were acquired with a digital camera.

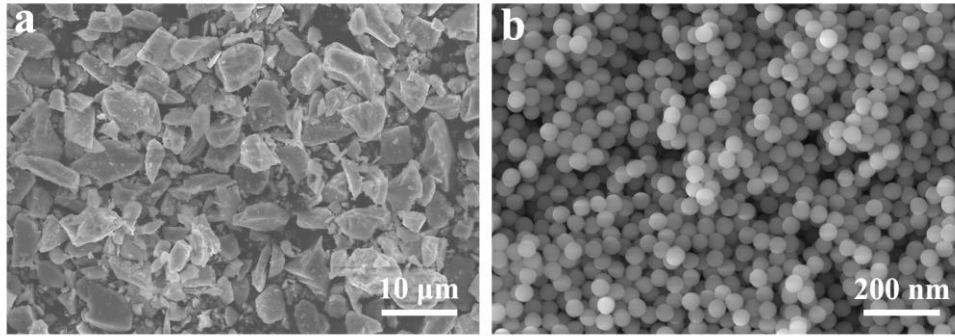


Figure S1. SEM images of a) Silicon bulk materials and b) Silica microspheres.

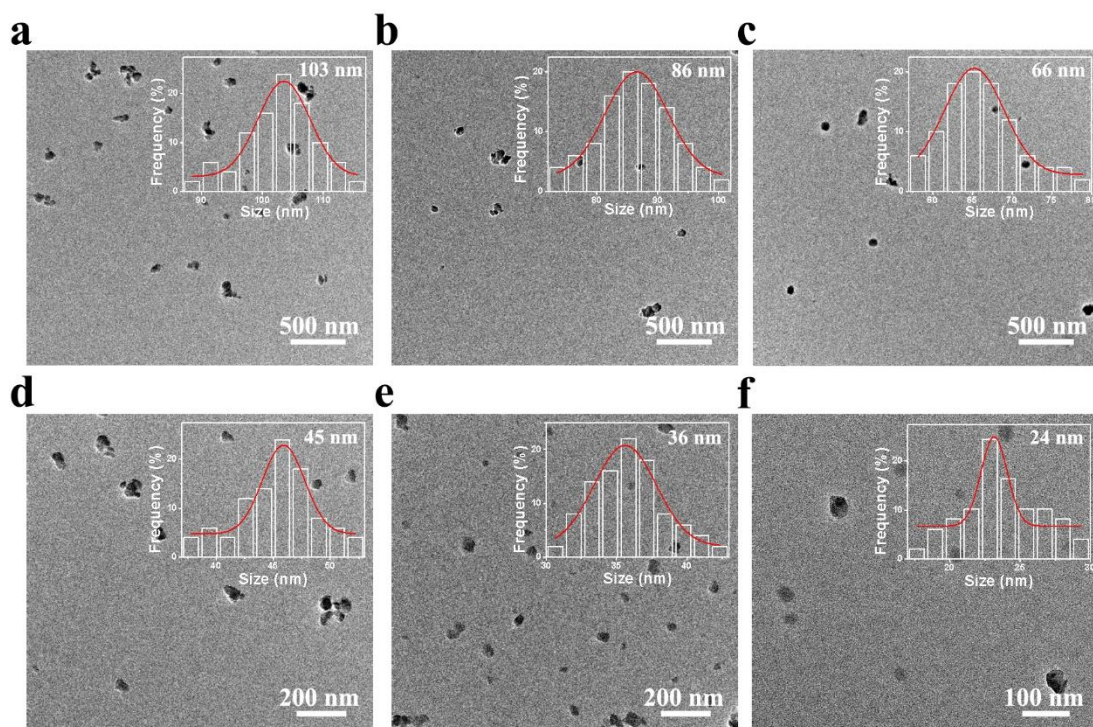


Figure S2. TEM images and corresponding lateral size distributions (insets) of the size-selected SiNPs.

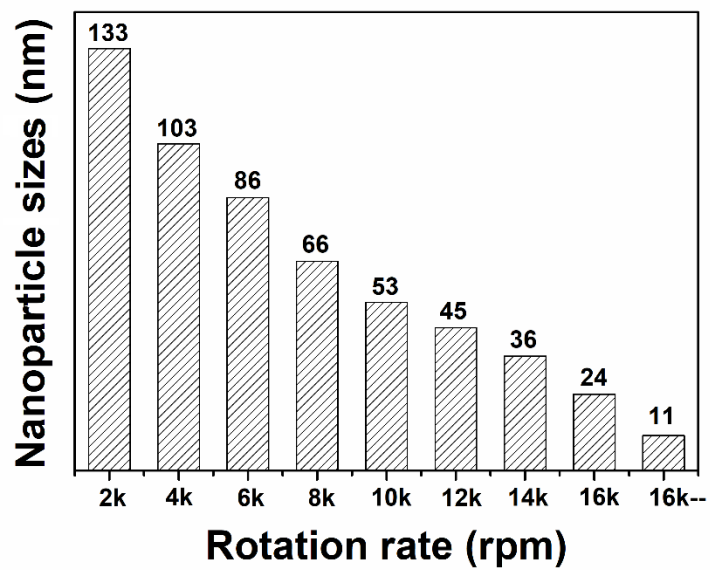


Figure S3. Size selection by cascade centrifugation.

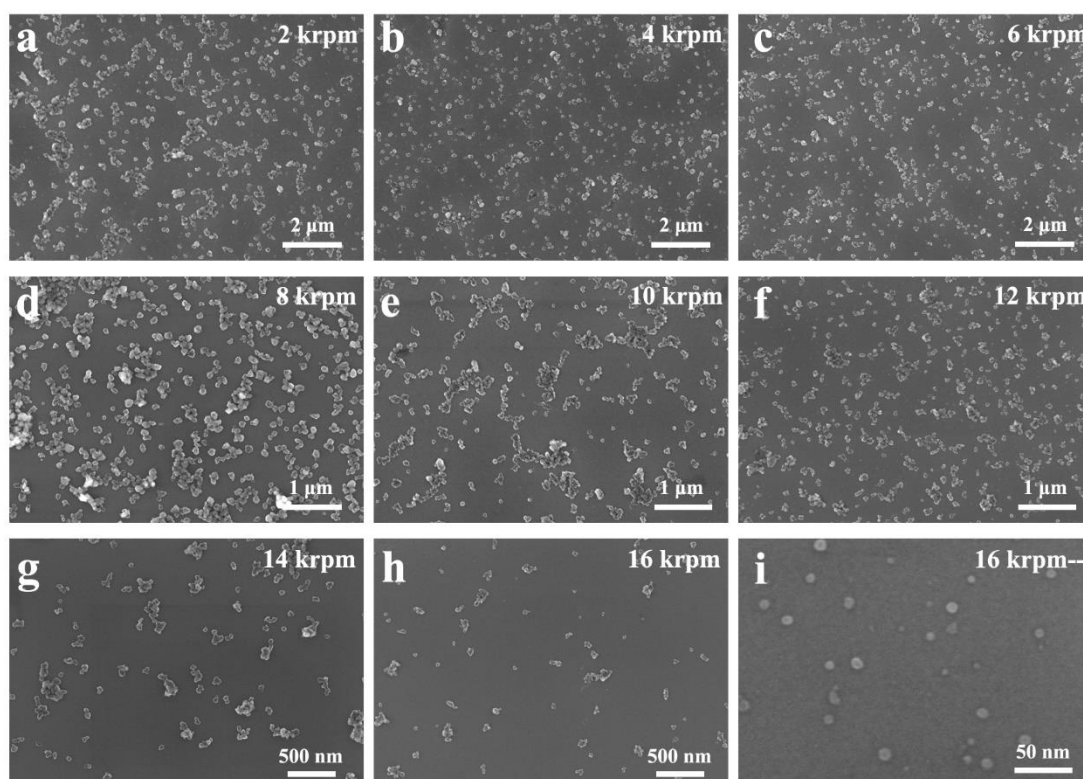


Figure S4. SEM images of the size-selected SiNPs.

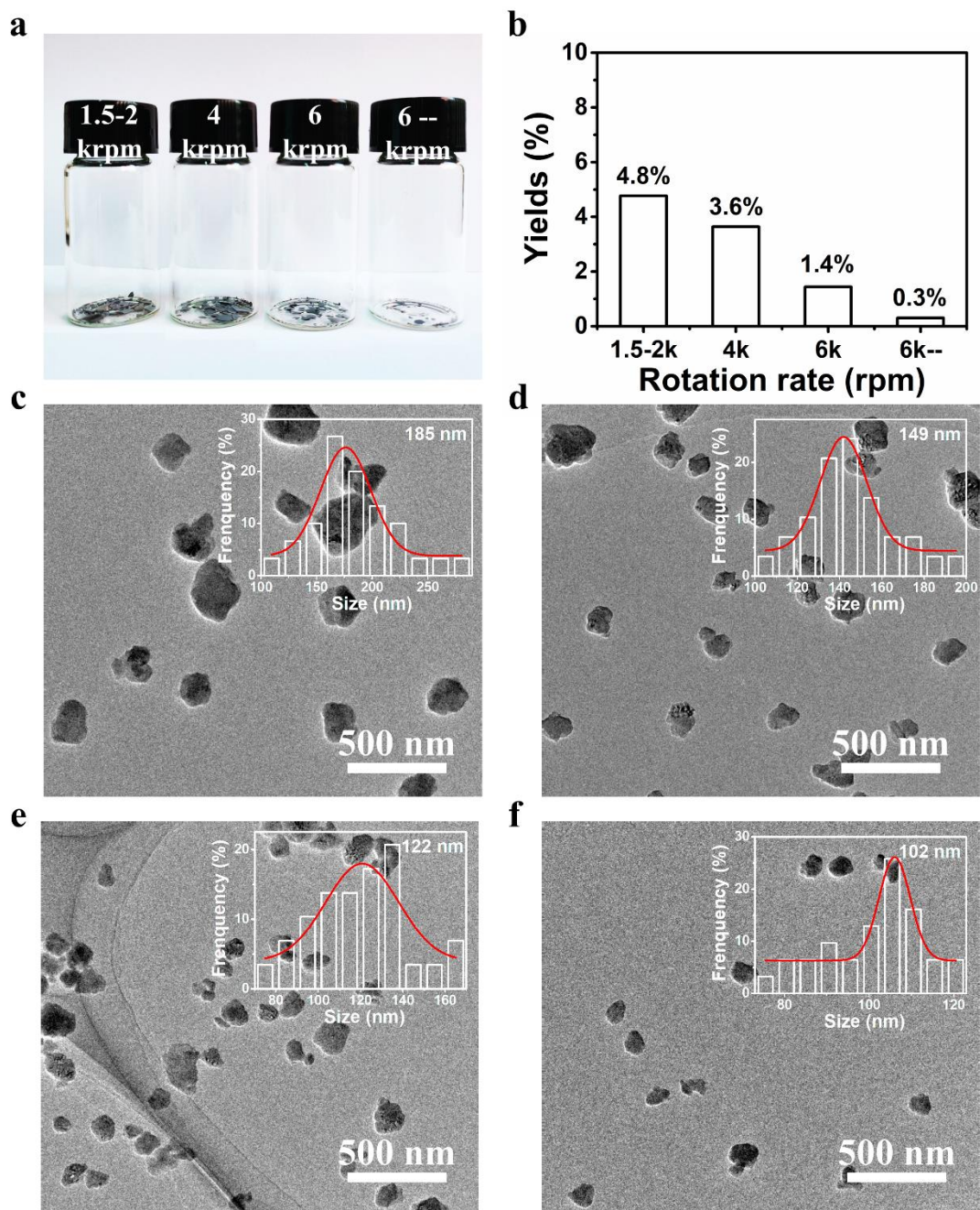


Figure S5. Si particles produced by simple ball-milling. a) Photographs of the as-produced Si particle powders. b) Yield evolution with varying rotation rate. c-f) TEM images of the as-produced particles (insets showing the lateral size distributions), the particle sizes were selected at cascade centrifugation rates of c) 2 krpm, d) 4 krpm, e) 6 krpm, and f) 6 krpm-, respectively.

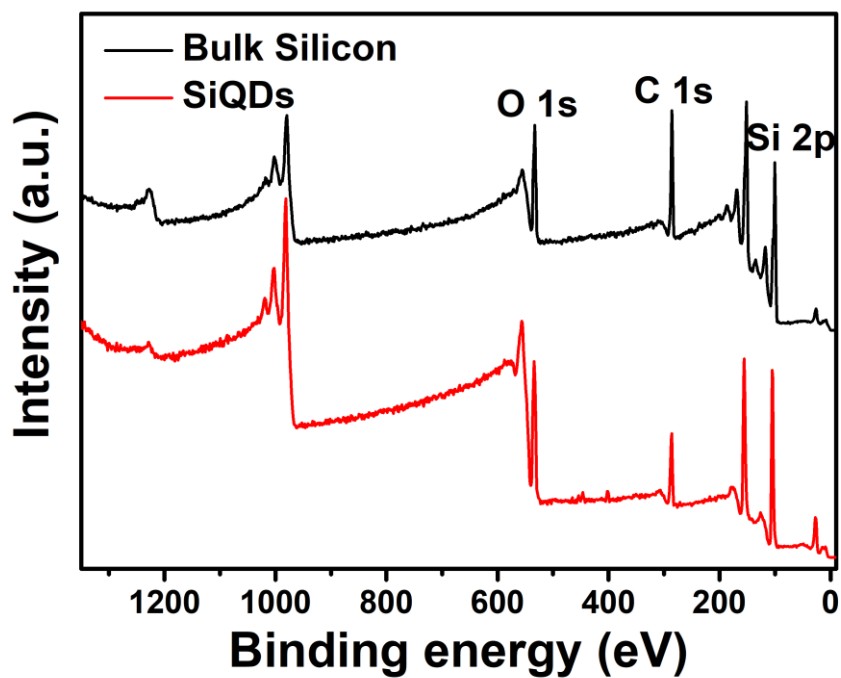


Figure S6. XPS full spectra of bulk Si and SiQDs.

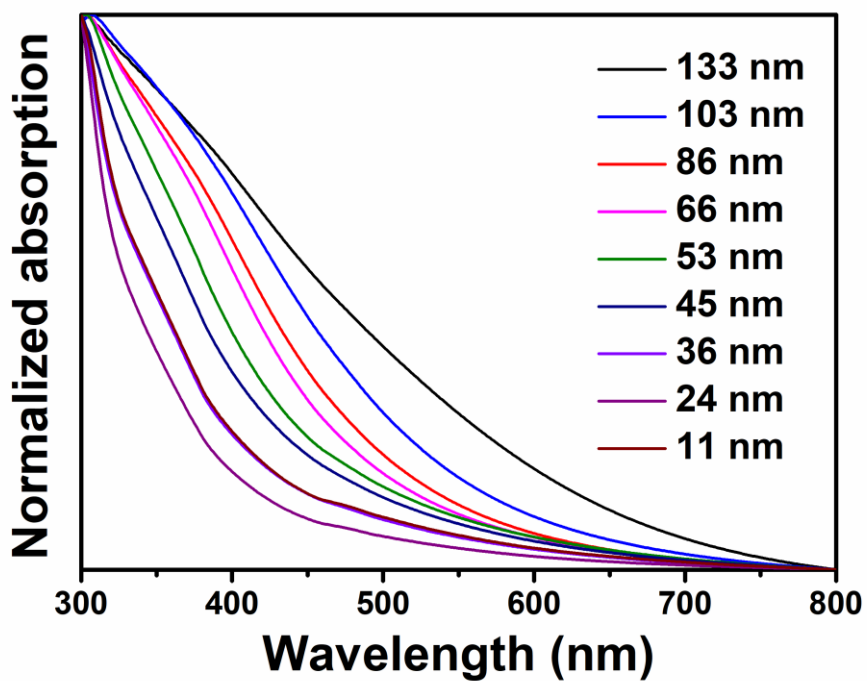


Figure S7. UV-vis absorption spectra of the size-selected SiNPs/NMP dispersions (0.1 mg/mL).

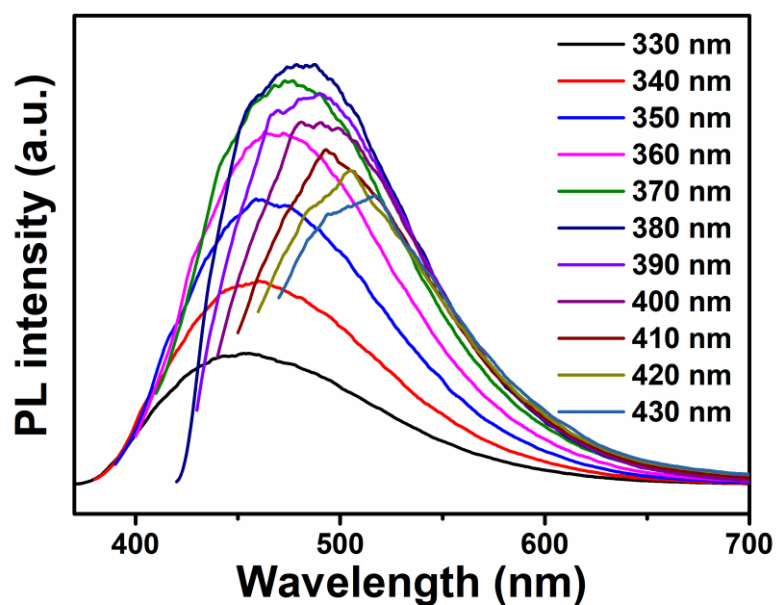


Figure S8. PL spectra of the SiQDs/NMP dispersions with varying excitation wavelengths. The concentration is fixed at 0.1 mg/mL.

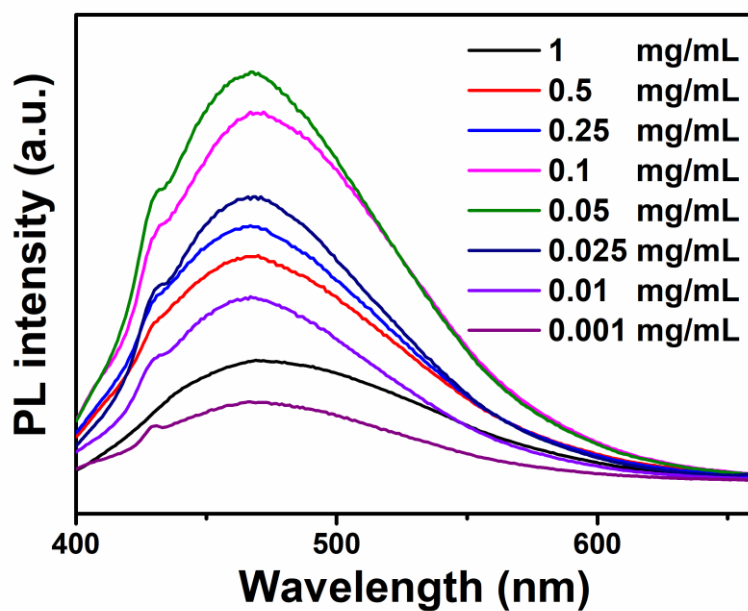


Figure S9. PL spectra of the SiQDs/NMP dispersions with varying concentrations. The excitation wavelength is 380 nm.

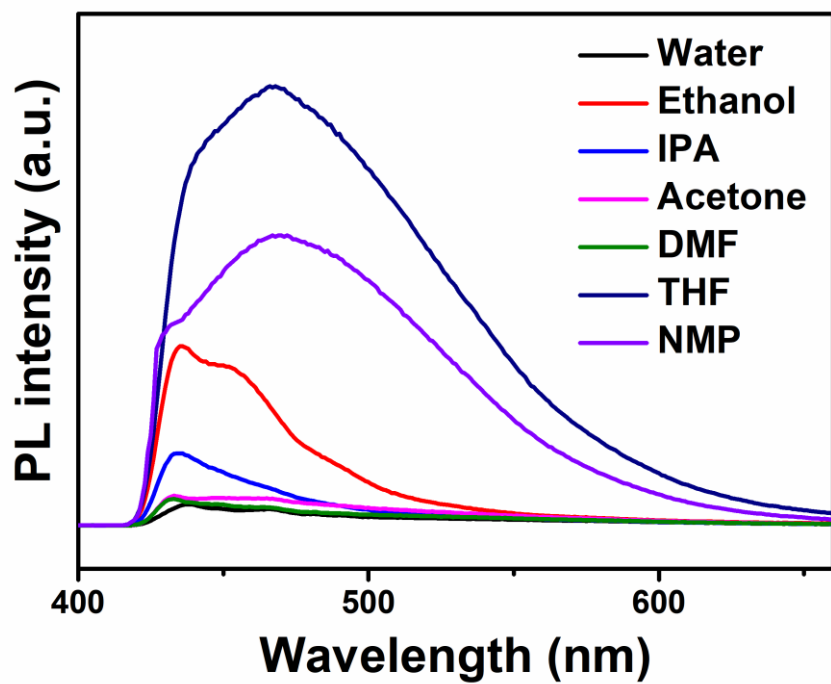


Figure S10. PL spectra of the SiQDs/NMP dispersions in varying solvents. The excitation wavelength is 380 nm. The concentration is fixed at 0.1 mg/mL.

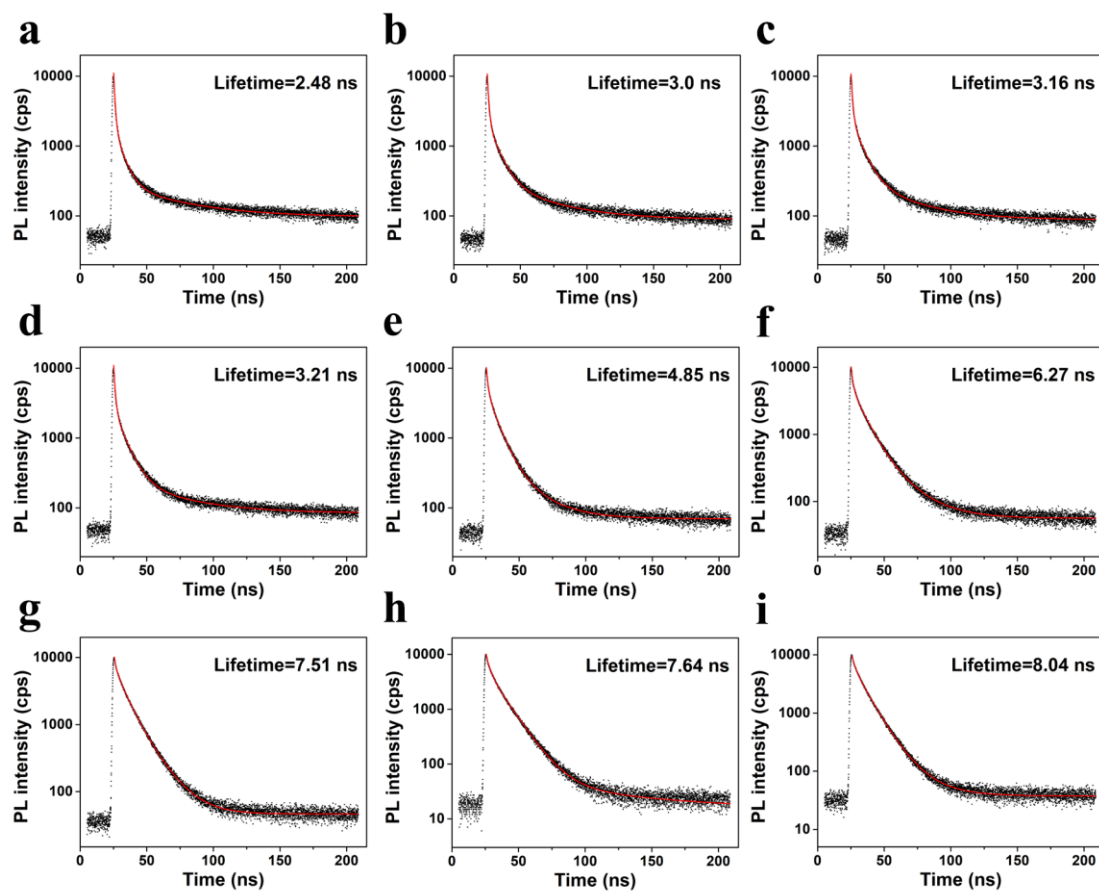


Figure S11. Time-resolved PL decay profiles of the size-selected SiNPs/NMP dispersions (0.1 mg/mL) upon 370 nm excitation wavelength.

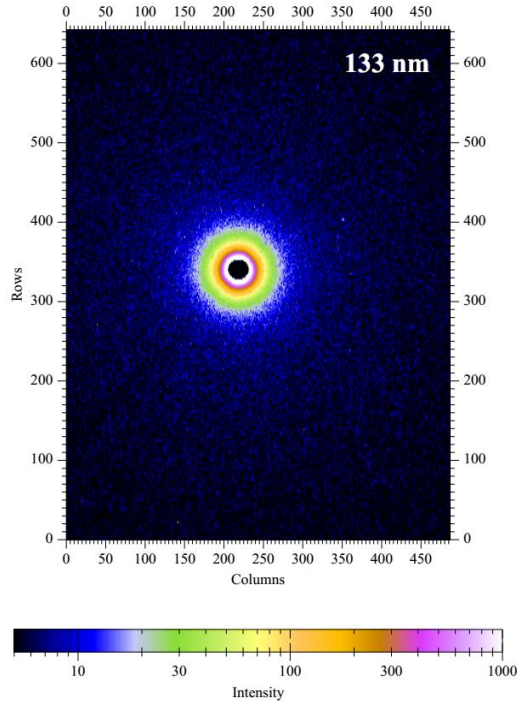


Figure S12. SAXS image of the hybrid thin film with the NPs of 133 nm.

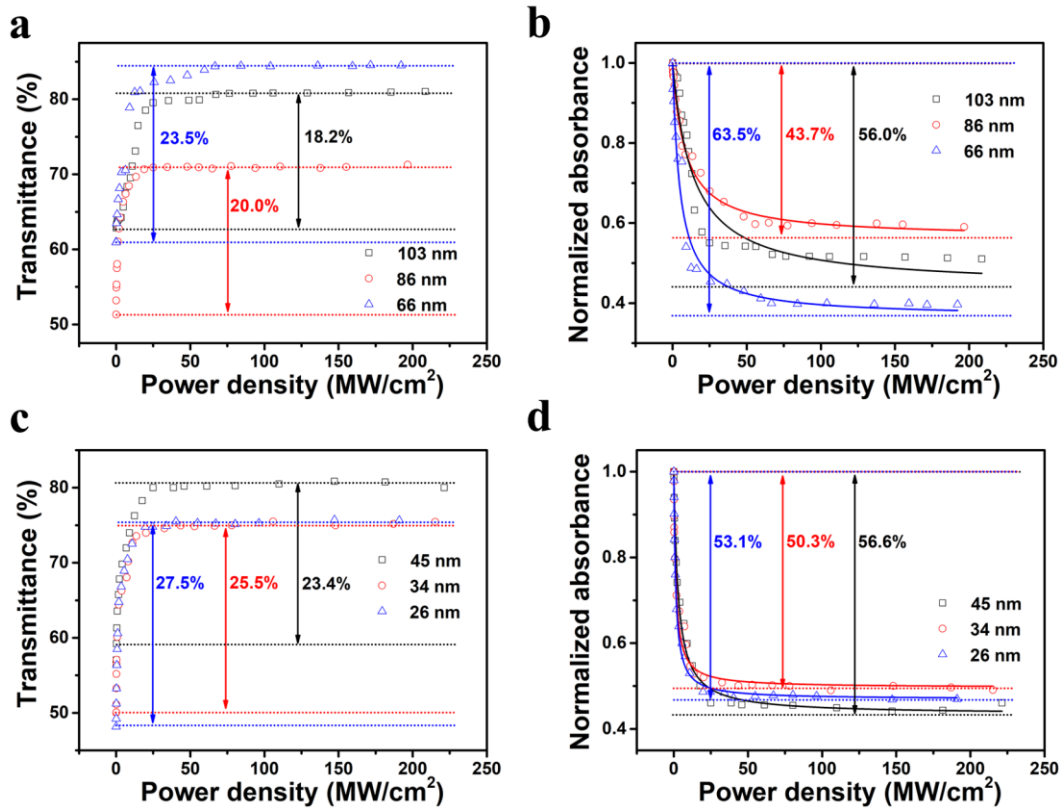


Figure S13. a, c) Nonlinear saturable absorption curves and b, d) normalized absorption curves of the SiNPs-PMMA hybrid thin films with varying NP sizes.

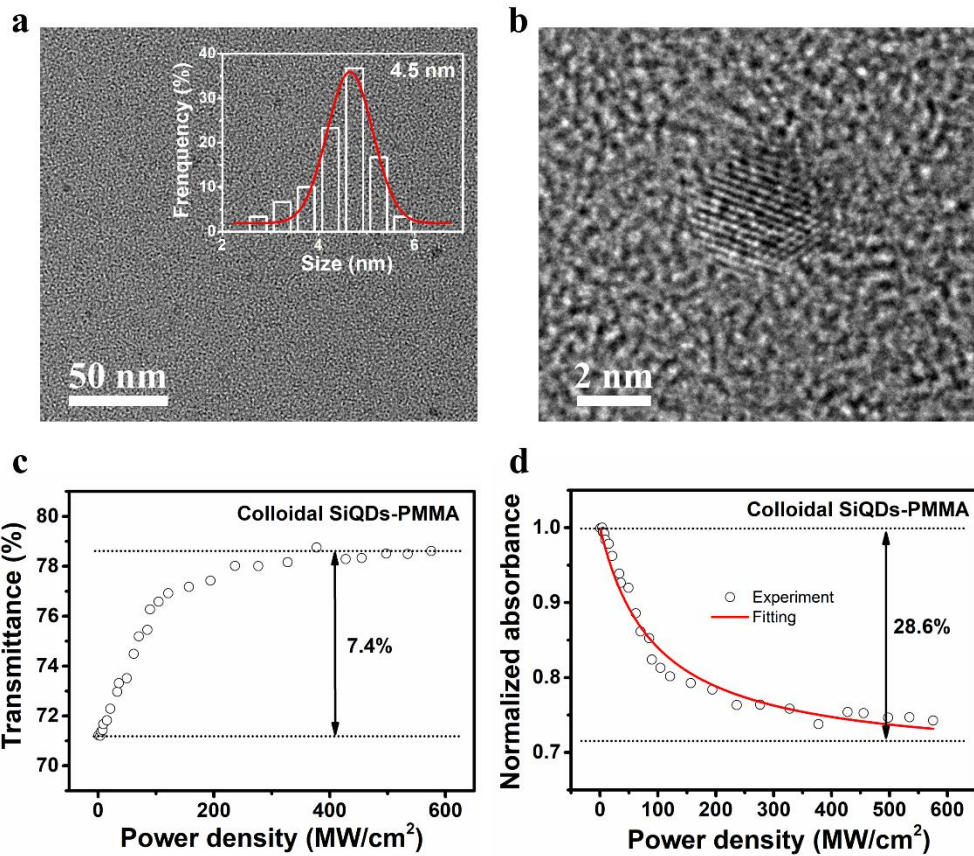


Figure S14. Solution-synthesized colloidal SiQDs and their NSA performances. a) TEM image of the colloidal SiQDs (inset showing the lateral size distribution). b) HRTEM image of an individual SiQD. c) Nonlinear saturable absorption curve. d) Normalized absorption curve. The hollow dots are the experimental data, and the solid curve is analytical fit to the data.

Table S1. Comparison of the PLQYs of SiNPs prepared via different methods

Methods	Diameter	PLQYs	References
Silica-assisted ball-milling and sonication-assisted solvent treatment	133 nm	2.9 %	<i>This work</i>
	53 nm	6.3 %	
	11 nm	9.8 %	
low temperature thermal	25 nm	6-9 %	6
one-step hydrothermal treatment	3.7 nm	31 %	7
Plasma synthesis	2 nm	70 %	8

References

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