
Supplementary information

3D-printed silica with nanoscale resolution

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Supplemental Information for

3D Printed Silica with Nanoscale Resolution

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1. TEM characterization of colloid Silica nanoparticles

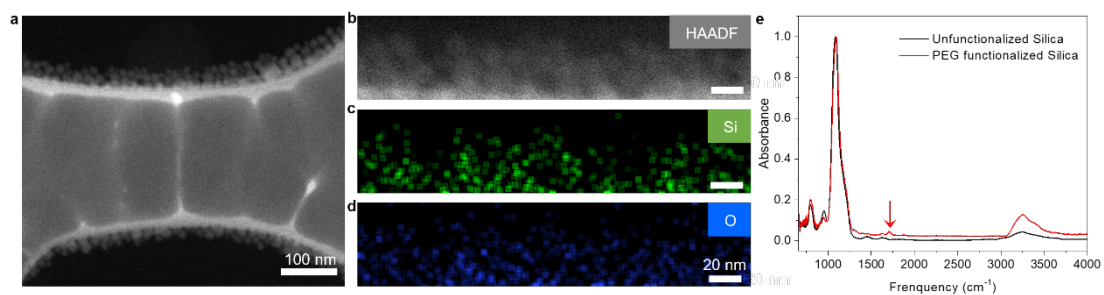


Figure S1. TEM observation (a, b) and EDS mapping (c,d) of the colloidal silica NPs. The silica NPs was synthesized via sol-gel method with average diameter of around 10 nm. e. FTIR spectra of unfunctionalized silica and PEG functionalized silica used in this work.

2. Small-angle X-ray scattering (SAXS) test

To verify the dispersity of silica NPs in nanocomposite ink, the mixture of polymer precursors and silica NPs (40 wt%) was measured and analyzed with SAXS. SAXS is a powerful tool to analyze the particle size¹, distribution^{2, 3}, and shape⁴ of macro-scale samples in a non-destructive way. The experiment was performed on a multi-purpose X-ray diffraction system (Regaku Smartlab X-Ray diffractometer) with a sealed copper X-ray tube operating at a voltage of 40 kV and a current of 44 mA. A Cross Beam Optics (CBO) mirror converts the divergent X-ray beam exiting the tube into a parallel beam and results in a monochromatic Cu K α radiation ($\lambda=0.154$ nm). The X-ray tube was in line focus and the system was configured in a classical Kratky line collimation mode for SAXS experiment. A scanning scintillation counter was used to collect the scattered X-ray intensities at different angles. Liquid samples were loaded into the system using borosilicate glass capillary tubes with a diameter of 0.5 mm and a wall thickness of 0.01 mm. It is noted that the photo-initiator was not added into the tested sample since it would trigger the polymerization of the precursors under ambient light. The polymer precursors were also tested for background subtraction.

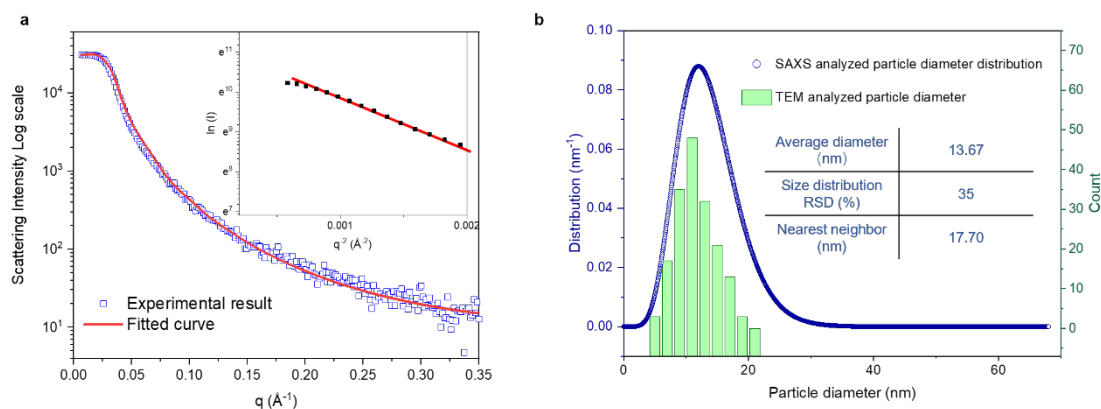


Figure S2. a. SAXS data and curve-fitting for the mixture of polymer precursors and functionalized silica NPs (40 wt%). Insert: Guinier diagram of SAXS data at low q . b. SAXS determined particle diameter distribution of functionalized silica NPs in polymer precursors and the TEM analyzed particle diameter of colloidal silica NPs.

Rigaku NanoSolver software was used to analyze the SAXS data. X-ray scattering from the polymer and the glass capillary tube was removed from the sample data as the background. A spherical model was used to fit the experimental data. In the calculation, size distribution was considered in addition to the form factor that accounts for the scattering from spherical particles. Because of the relatively high silica concentration in the polymer, a structure factor that takes into account the possible correlation between the nanoparticles was also considered. The SAXS curve with background subtracted was well fitted, shown in Fig. S2a. The distribution of silica NPs could be calculated, as shown in Fig. S2b. The average diameter is 13.67 nm and the size distribution RSD is 35%, which is consistent with the TEM analyzed particle diameter distribution as plotted by a histogram in Fig. S2b. The nearest neighbor distance is 17.7 nm and the Guinier curve shows a linear trend at low q , indicating limited aggregation⁵. Overall, the SAXS data provide a strong evidence that the functionalized silica NPs are well-dispersed in nanocomposite ink.

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macromolecular structures, conformations and assemblies in solution. Quarterly reviews
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3. STEM, XRD, XPS and Raman characterization of the printed materials

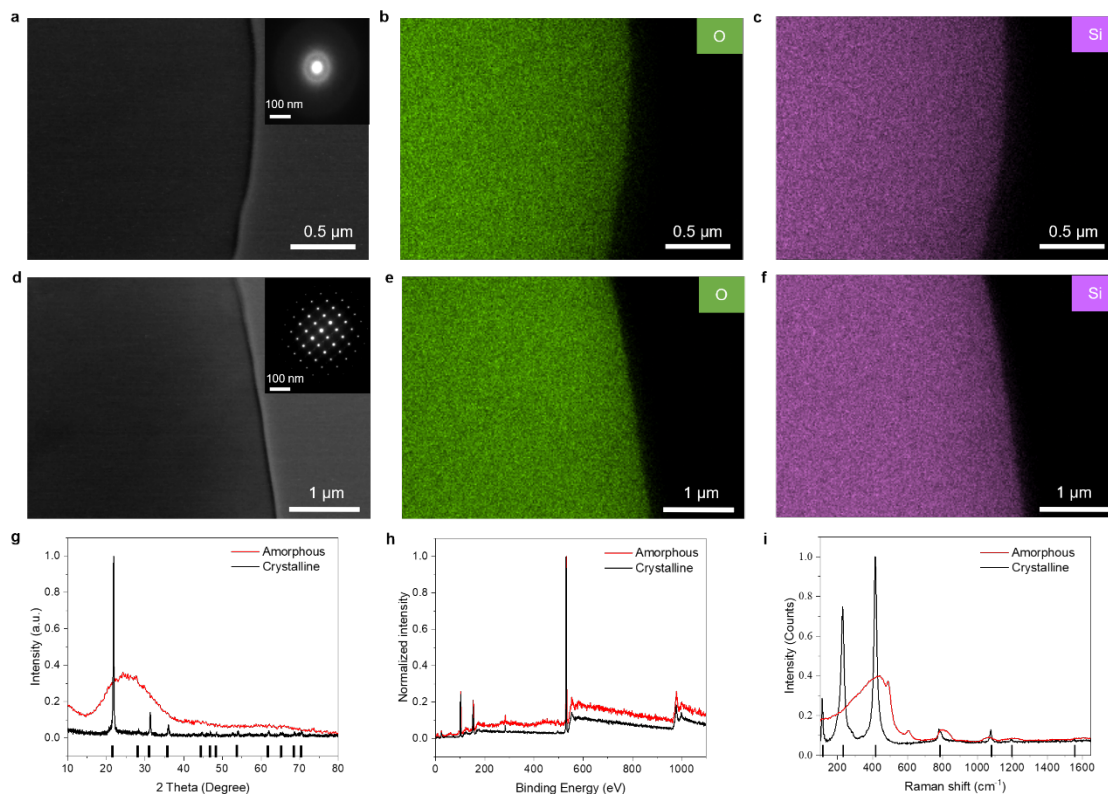


Figure S3. a. Bright field STEM image and diffraction pattern of printed amorphous silica. b. EDS mapping of O of printed amorphous silica. c. EDS mapping of Si of printed amorphous silica. d. Bright field STEM image and diffraction pattern of printed crystalline silica. e. EDS mapping of O of printed crystalline silica. f. EDS mapping of Si of printed crystalline silica. g. X-ray diffraction. h. X-ray photoelectron spectroscopy. i. Raman spectroscopy of printed amorphous and crystalline silica.

4. Additional printed 3D structures under optical microscope

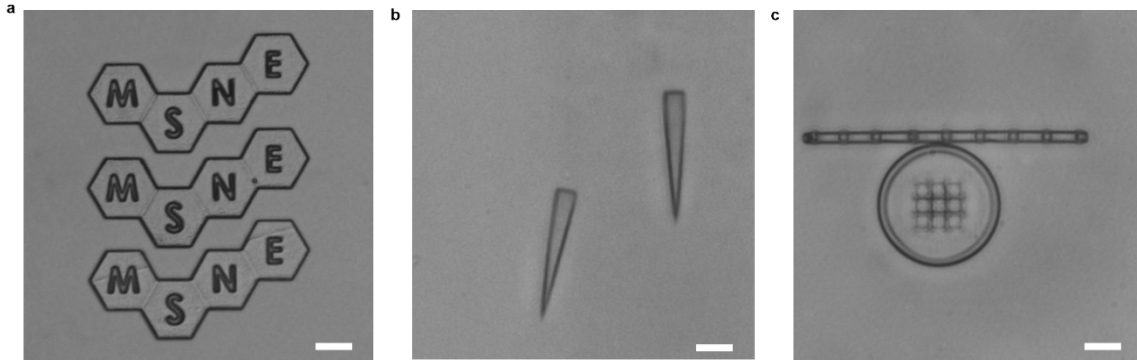


Figure S4. Printed silica objects under optical microscope. *a.* MSNE department logos, scale bar: 5 μm .
b. Side-lying isolated micro needles, scale bar: 10 μm . *c.* Suspended ring resonator with truss support and suspended waveguide, scale bar: 5 μm .

5. Ring resonator Q value measurement

To optically characterize the fabricated micro-disk and vertical micro-toroid cavities, we used the setup shown in Fig. S5 to measure the transmission spectrum. A biconically tapered fiber with waist diameter of about 1.5 μm was fabricated by immersing into 48% hydrofluoric acid for 70 minutes, which provided efficient coupling with the cavities. For the optical measurements, a single-mode tunable laser (Ando AQ4321D, 1520 nm - 1620 nm) was initially launched into the tapered fiber and used to evanescently excite the whispering gallery modes (WGMs) in the micro-disk and vertical micro-toroid cavities. The tunable laser was periodically scanned within 1540 nm to 1570 nm with step size of 20 pm to measure the transmission spectrum. And the polarization of the light was adjusted by using the fiber polarization controller to enhance or suppress the TE/TM polarized WGMs. The transmitted light was then collected by a photodetector (Multi-Function Optical Meter 1835-C, Newport). The data was subsequently imported into the computer to generate the transmission spectrum curve. The tapered fiber was attached and precisely aligned by a three-axis micromanipulator with a resolution of 100 nm to approach the resonator. One camera (InGaAs SWIR SU320KTS-1.7RT, Goodrich) attached on microscope with an objective lens (Plan Fluor 20X/0.45, Nikon) from the top and another camera (ImagingSource DFK 72BUC02) with an objective lens (10X/0.30, Nikon) from

the side were used to monitor their relative positions and the coupling state. After carefully adjusting the relative positions of the tapered fiber and the cavity, the WGMs could be efficiently excited and the transmission spectrum was then collected by the photodetector.

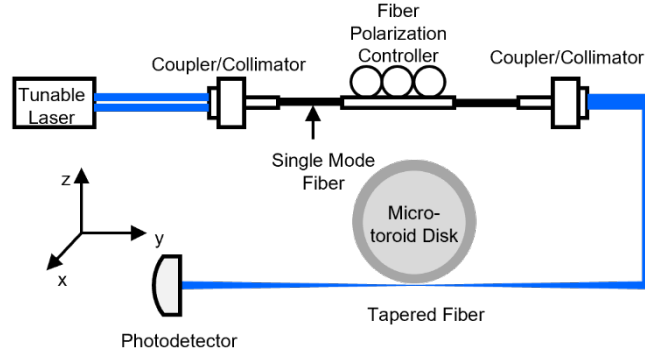
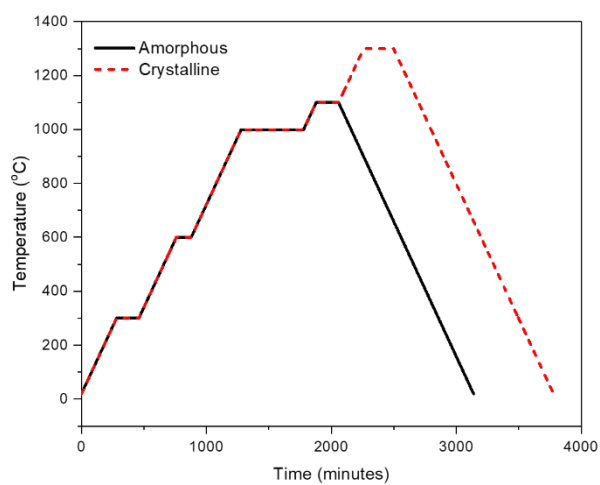


Figure S5. Optical setup sketch measuring Q value of printed micro resonators.

The measured normalized transmission spectrum of the fabricated micro-toroid resonator is shown in Fig. 3b. The Q factor is defined by $Q = \lambda/\Delta\lambda$, where λ is the resonance wavelength and $\Delta\lambda$ is the FWHM (full width at half maximum). The Q factor is calculated by measuring the line width/FWHM of the Lorentzian-fitted resonance in the transmission spectrum as shown in Fig. 3c. According to the measured FWHM of the resonator, the calculated Q value is about 11000, which is limited by material loss and surface scattering and can be further improved by optimizing the fabrication process and light coupling setup.

128 **6. Pyrolysis and Sintering process**



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130 **Figure S6.** The temperature vs time diagram of the pyrolysis and sintering processes