Supporting Information for

Controllable Fabrication of Novel All Solid-State PbS Quantum Dot-doped Glass Fibers with Tunable Broadband Near-infrared Emission

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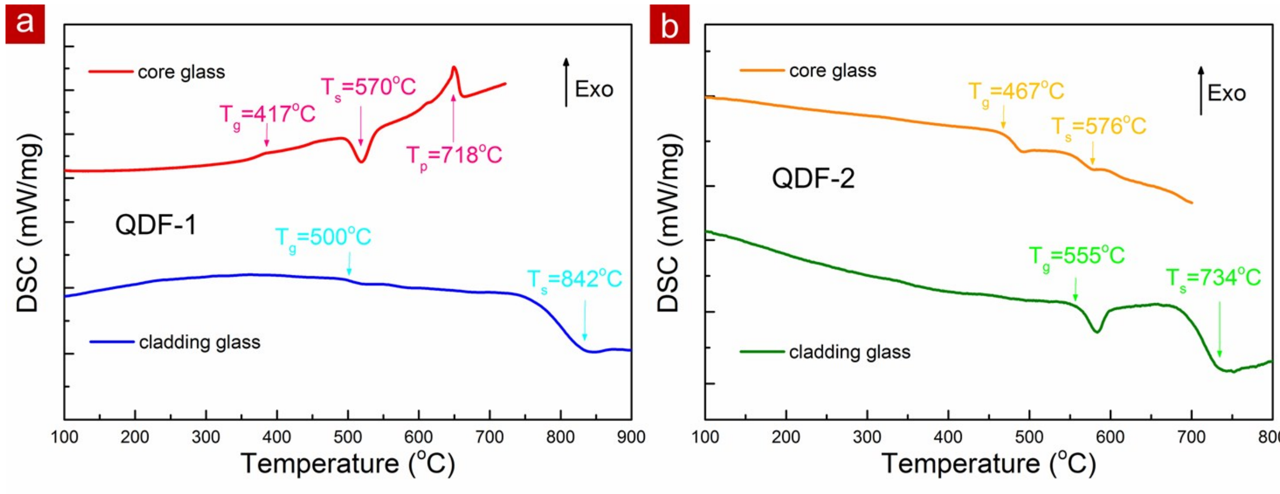

Figure S1. DSC curves of the as-prepared bulk glass for fiber core and cladding. (a)The glass transition temperature (T_g) of QDF-1 core and cladding glass was at 417 and 500 ^oC, and the softening temperature (T_s) was at 570 and 842 ^oC, respectively. So, fiber QDF-1 was drawn at 1000 ^oC eventually. (b)The glass transition temperature (T_g) of QDF-2 core and cladding glass was at 467 and 555 ^oC, and the softening temperature (T_s) was at 576 and 734 ^oC, respectively. And fiber QDF-2 was drawn at 950 ^oC.

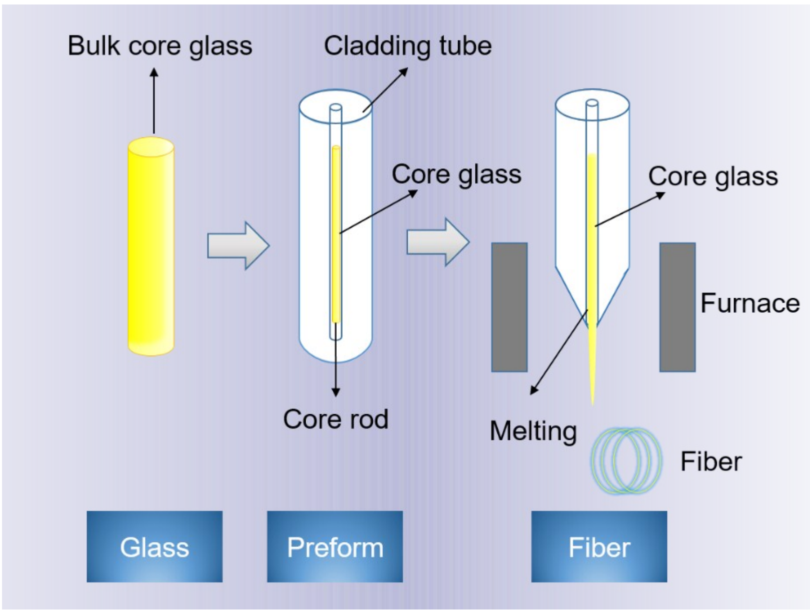

Figure S2. Schematic diagram of novel "melt-in-tube" technique. Firstly, the core bulk glass was prepared by conventional melt-quenching technique. The bulk glass was cold worked into cylindrical rods and inserted into the cladding glass tube. The bottom of glass tube was sealed to form a preform. The preform was drawn into fibers quickly. During the fiber-drawing process, the cladding (high melting-point glass) underwent a softening process, while the core (low melting-point glass) underwent a glass melting process. Owing to the high cooling speed of thin fiber core, the core glass maintained amorphous state easily.

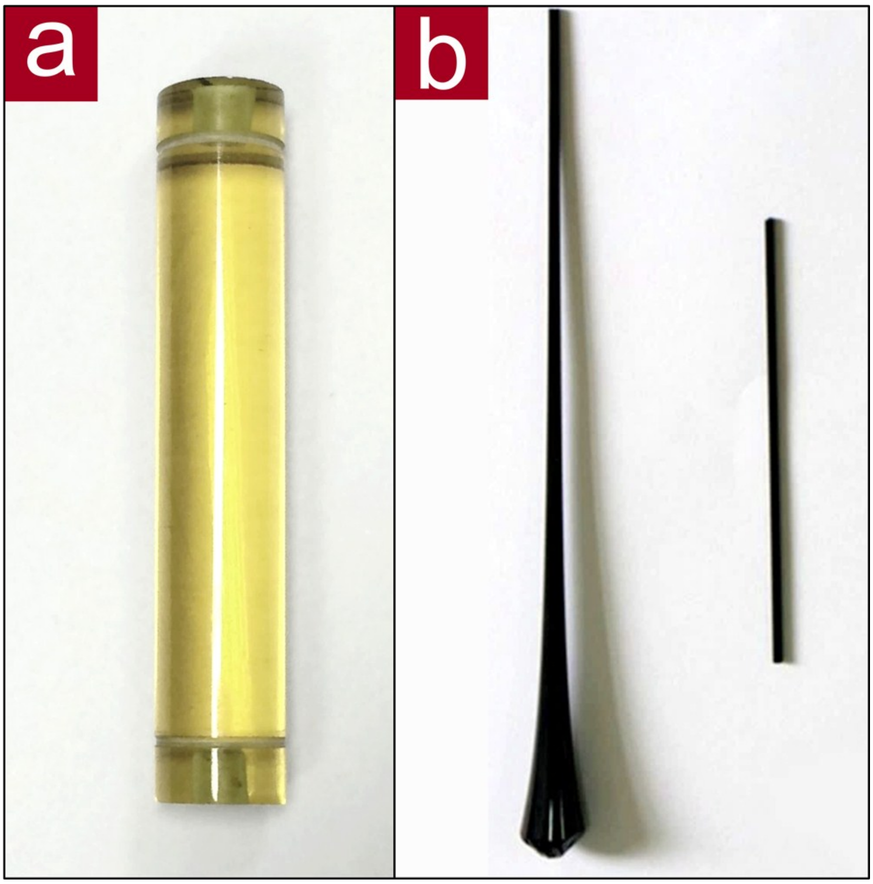

Figure S3. Images of glass preform before (a) and after (b) drawing by traditional rod-in-tube technique. The drawing temperature of quantum dot (QD)-doped glass rod was about 630 ^{o}C. Before drawing process, the glass rod was transparent. However, the glass rod turned to dark and opaque after drawing process, resulting in high transmission loss and fluorescence quenching. Thus, the traditional rod-in-tube technique is not suitable for fabricating QD-doped glass fibers.

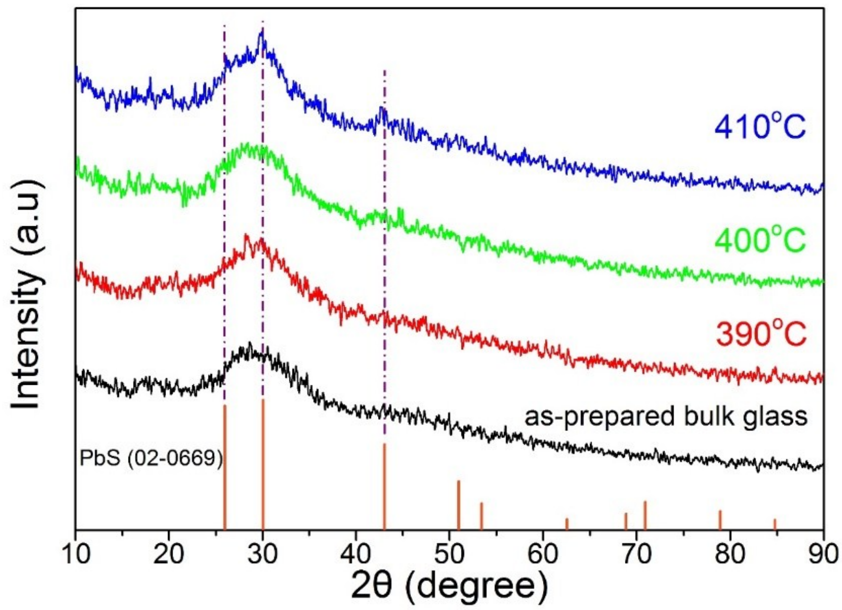

Figure S4. XRD patterns of as-prepared bulk glass QDG-1 for fiber core and bulk PbS QD-doped glasses heat treated at different temperatures for 5 hours. For the as-prepared bulk glass, the pattern presented as broad band without any sharp peak. While, for the PbS QD-doped glasses, several sharp peaks appeared besides the amorphous broad band in the XRD patterns. The sharp peaks matched well with the diffraction peaks of PbS (ICDD PDF No. 02-0669) crystal. The main characteristic peaks at $2\theta=25.9$, 29.9, 42.9, 50.8 and 53.3^{o} were attributed to the diffractions of the (111), (200), (220), (311) and (222) crystal facets of PbS QDs, respectively.

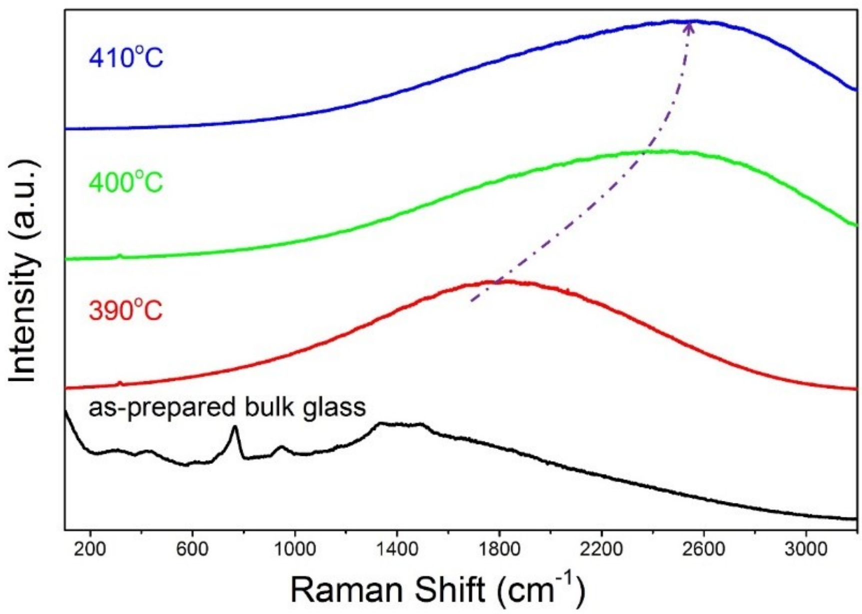

Figure S5. Micro-Raman of as-prepared glass QDG-1 and QDG-1 heat treated at different temperatures for 5 hours. The Raman spectrum of as-prepared glass QDG-1 exhibited four main bands around 1483, 1330, 945 and 765 cm^{-1}, which corresponded to the characteristic Raman bands of borate glass. The Raman spectra of glass QDG-1 heat treated at different temperatures presented as intense broad bands. And Raman bands of borate glass were concealed. The broad bands were attributed to the fluorescence background resulting from the PbS QDs.[1] With the heat treated temperature increasing from 390 to 410 ^{o}C, the center of the broad bands shifted from 1803 to 2583 cm^{-1} due to the growth of PbS QDs in sizes.

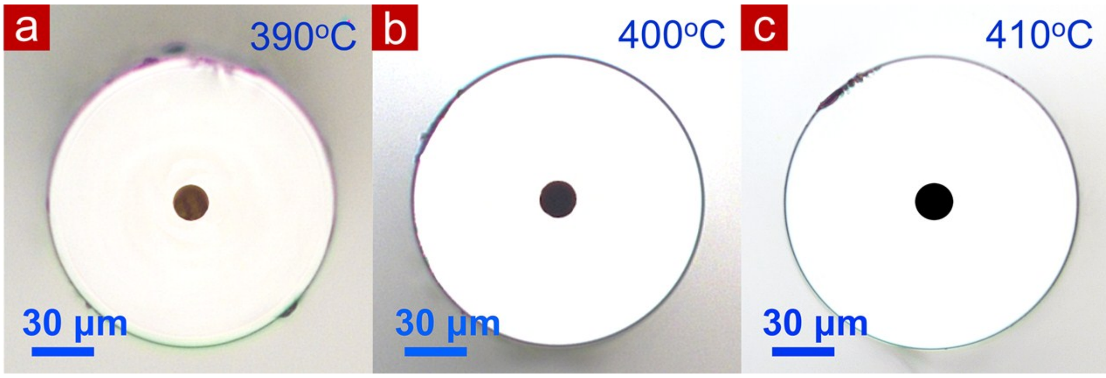

Figure S6. a-c) the images of cross section of fiber QDF-1 heat treated at different temperature for 5h.

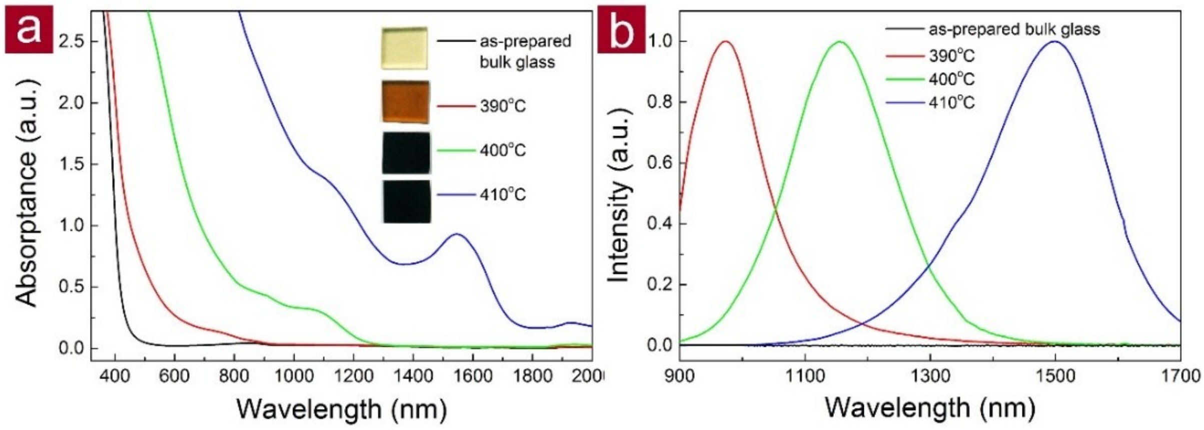

Figure S7. (a) Absorption spectra of as-prepared glass QDG-1 and QDG-1 heat treated at different temperatures for 5 hours. The inset of figure (a) was the images of as-prepared glass QDG-1 and QDG-1 heat treated at different temperatures. As-prepared QDG-1 presented pale yellow, and glass QDG-1 got darken with increasing the heat treatment temperature. It is also noticed that no absorption band was observed between 400 and 2000 nm in the absorption spectra of as-prepared glass QDG-1. When the glass was heat treated at 390 ^{o}C for 5 h, the absorption edge of glass shifted to longer wavelength, and a weak absorption band centered at ~750 nm appeared in the absorption spectrum. The absorption band was ascribed to the generation of electron-hole pairs of PbS QDs induced by the excitation photon. When the heat treatment temperature further increased to 400 ^{o}C and 410 ^{o}C, the absorption band of PbS QDs gradually shifted to longer wavelength, which confirmed that the size of PbS QDs grew continuously with the increase of temperature. The intensity of the absorption band was also enhanced with the increase of temperature, indicating that the number density of PbS QDs in glass matrix also increased when the heating temperature increased from 390 to 410 ^{o}C.

As presented in figure S6. (b), excited by 808 nm laser, no emission band was observed in the photoluminescence (PL) spectrum of as-prepared bulk glass. However, for glass QDG-1 heat treated at different temperatures, broadband near-infrared emissions were observed in the PL spectra, which were attributed to the recombination of electron-hole pairs of PbS QDs. For glass QDG-1 heat treated at 390, 400 and 410 ^{o}C, the wavelength-center of the emission band located at 970, 1160 and 1500 nm, respectively. And the full width at half-maximum (FWHM) was about 142, 193 and 222 nm, respectively. With increasing heat treatment temperature, the PbS QDs in glasses grew up and the size distribution became wider, resulting in the red-shift and broaden of the PL emission band.

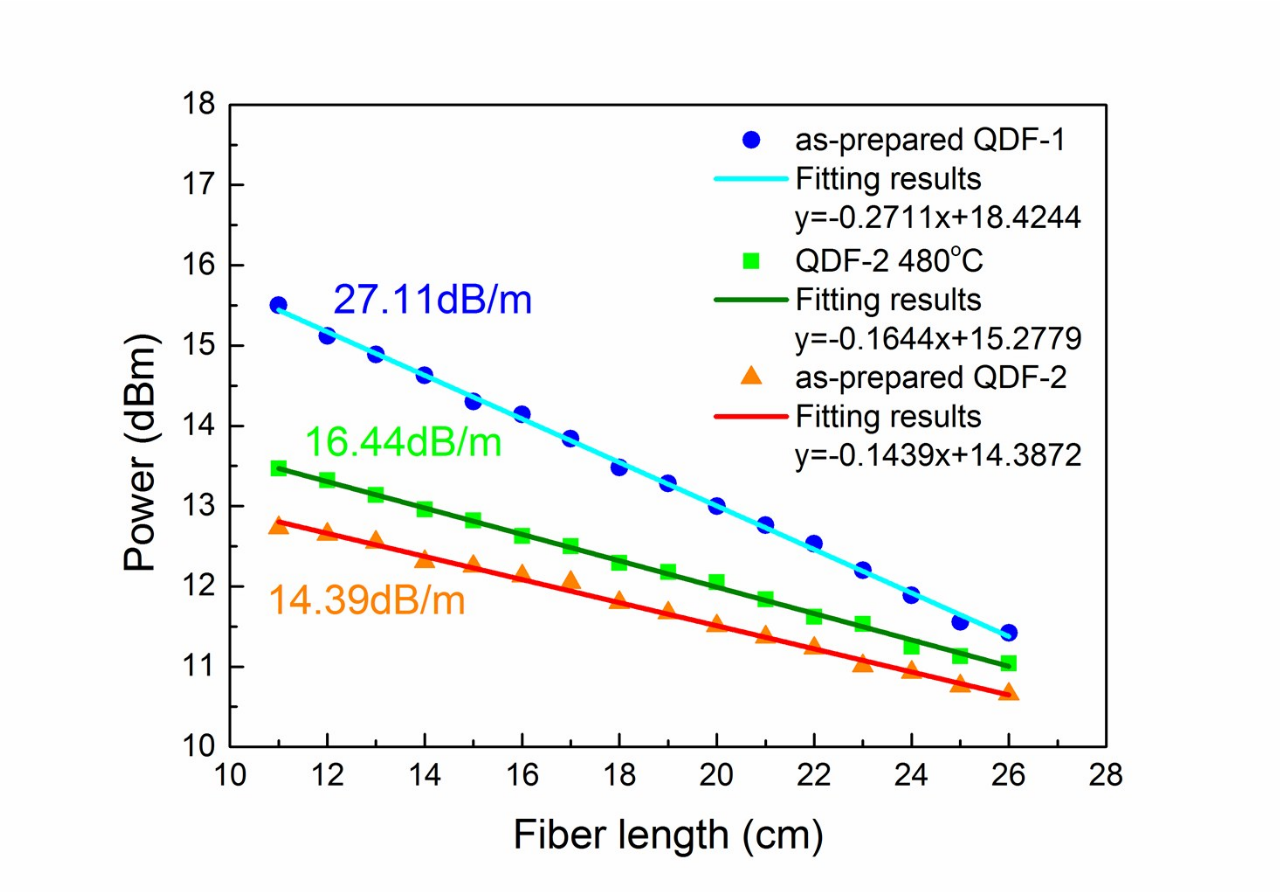

Figure S8. Cutback measurement of as-prepared fiber QDF-1 and QDF-2 and fiber QDF-2 heat treated at 480 ^{o}C. The transmission losses of as-prepared fiber QDF-1 and giber QDF-2 at 1310 nm was measured to be 27.11 dB/m and 14.39 dB/m, respectively. The transmission loss was reduced 46.9% after optimization of composition and thermal expansion of fiber core and cladding glass. The transmission loss of fiber QDF-2 increased to 16.44 dB/m after heat treated at 480 ^{o}C for 5h.

References

1 S. Fan, G. Wu, H. Zhang, Y. Yu, J. Qiu and G. Dong, *J. Mater. Chem. C*, 2015, **3**, 6725.