Supplementary Information (SI) for Journal of Materials Chemistry C.

Superconductivity above 30 K due to the introduction of oxygen element in CaFeAsF

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Supplementary information

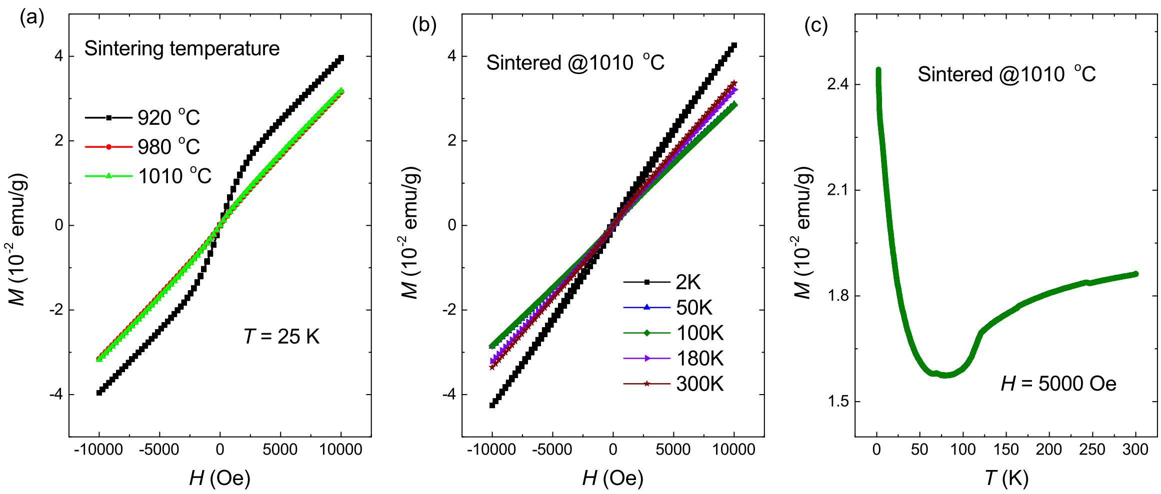

Figure S1 Magnetization of the pristine polycrystalline CaFeAsF samples. (a) Field dependence of magnetization of polycrystalline CaFeAsF samples sintered at different temperatures. The sintering time was fixed at 40 hrs. The data were measure at 25 K. When the sintering temperature is relatively low, such as 920 ^{o}C, the M-H curve shows significant nonlinearity, indicating the presence of ferromagnetic impurities in the sample. The samples sintered at 1010 ^{o}C were chosen to carry out the following annealing experiments. (b) Magnetization as a function of magnetic field for the sample sintered at 1010 ^{o}C. (c) Temperature dependence of magnetization for the sample sintered at 1010 ^{o}C. The M-T curve reveals a transition at around 121 K which is a characteristic of the structural transition, being consistent with the resistance data of single-crystalline sample (see Fig. 2(a) in the main text) and our previous report[1].

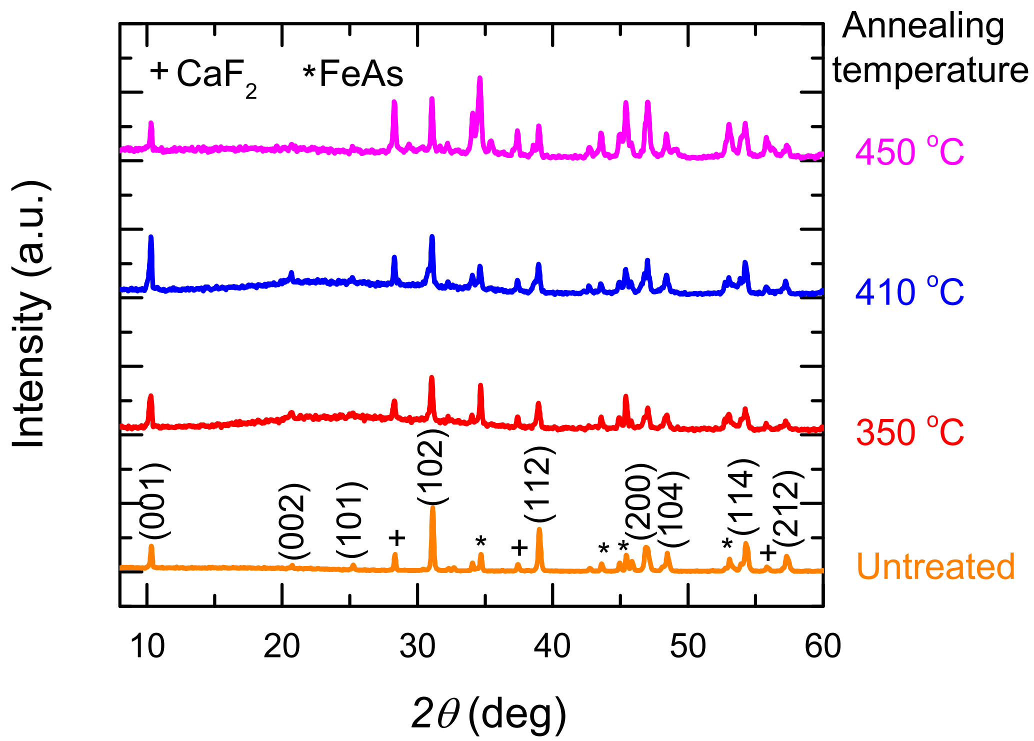

Figure S2 X-ray diffraction patterns of the polycrystalline CaFeAsF samples annealed under three typical conditions. The data of untreated sample is also shown for a comparison. Besides the main phase of CaFeAsF, CaF_2 and FeAs serve as two notable impurity phases, the amount of which increases with the enhancement of annealing temperature.

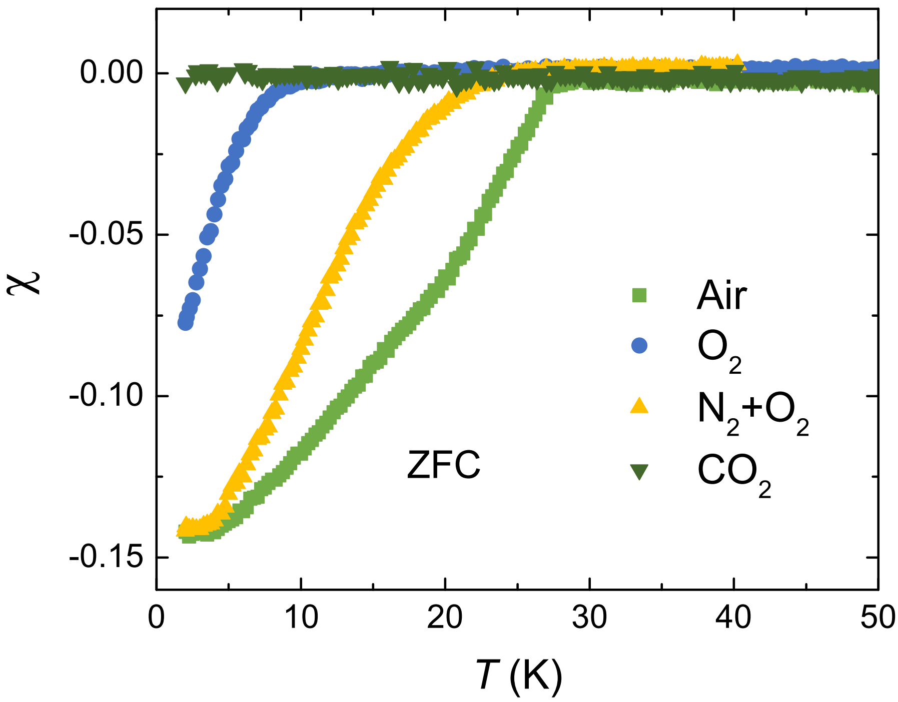

Figure S3 Magnetic susceptibility data of CaFeAsF single crystals annealed in different atmospheres under the zero-field-cold mode (ZFC) as a function of temperature. The mixture ratio of nitrogen (N_2) and oxygen (O_2) gases mimics the ratio in air. For different atmospheres, the annealing temperatures and the holding time remain the same: at 330 ^{o}C for 18 hrs. The results indicate that the introduction of oxygen element during the annealing process may be a key factor in the generation of superconductivity.

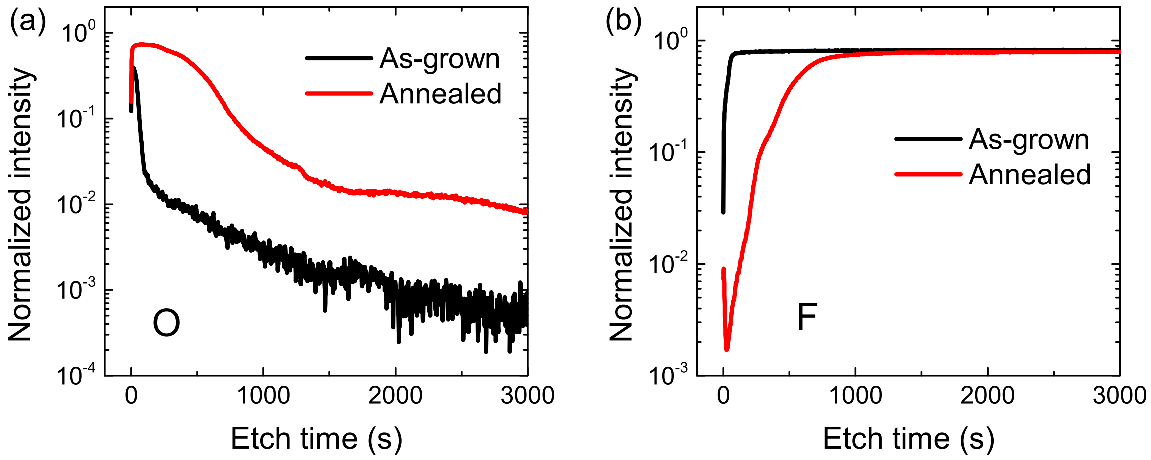

Figure S4 A graph of the data in figures 4(a) and (b) in the main text, drawn in a different form to facilitate a more comprehensive comparison of as-grown and annealed samples. (a) Normalized intensity of O element as a function of the etch time, which is a indicator for the depth from samples surface, for the as-grown and annealed samples from the TOF-SIMS measurements. (b) Normalized intensity of F element as a function of the etch time for the as-grown and annealed samples from the TOF-SIMS measurements.

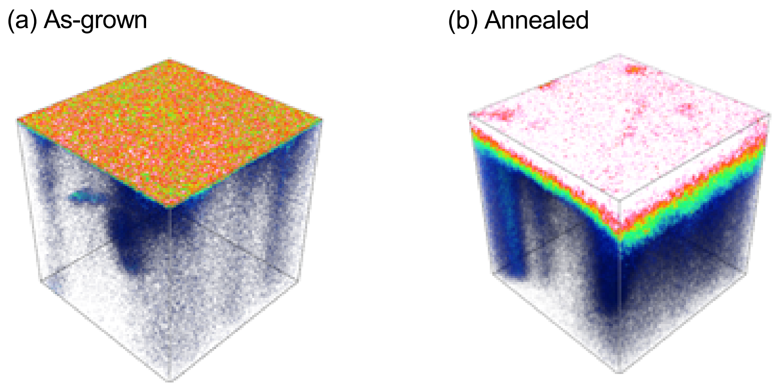

Figure S5 The three-dimensional images of the TOF-SIMS intensity (unit: counts) of oxygen element for the as-grown (a) and annealed (b) samples respectively.

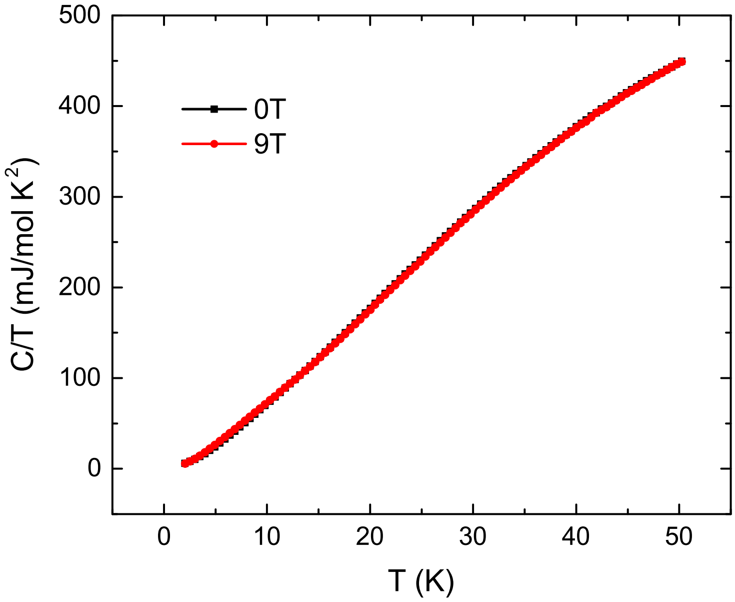

Figure S6 Low-temperature specific heat of air-annealed CaFeAsF single crystal under magnetic field of 0 T and 9 T. The field is applied vertical to the sample surface. No SC feature can be observed in the specific heat data.

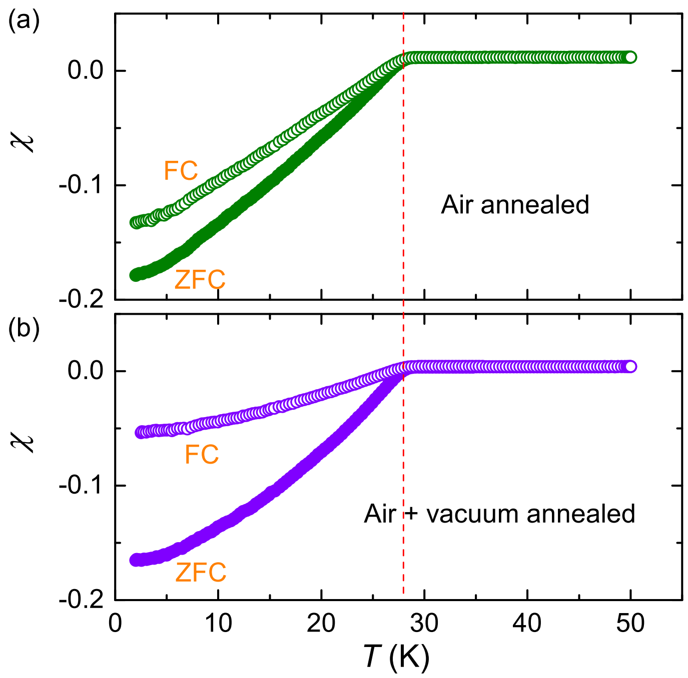

Figure S7 Effect of post-vacuum-annealing on the superconductivity of air-annealed polycrystalline CaFeAsF. Magnetic susceptibility of air-annealed polycrystalline CaFeAsF with (a) and without (b) a post-vacuum-annealing treatment. The red dashed vertical line is a guide for eyes for the position of SC transition.

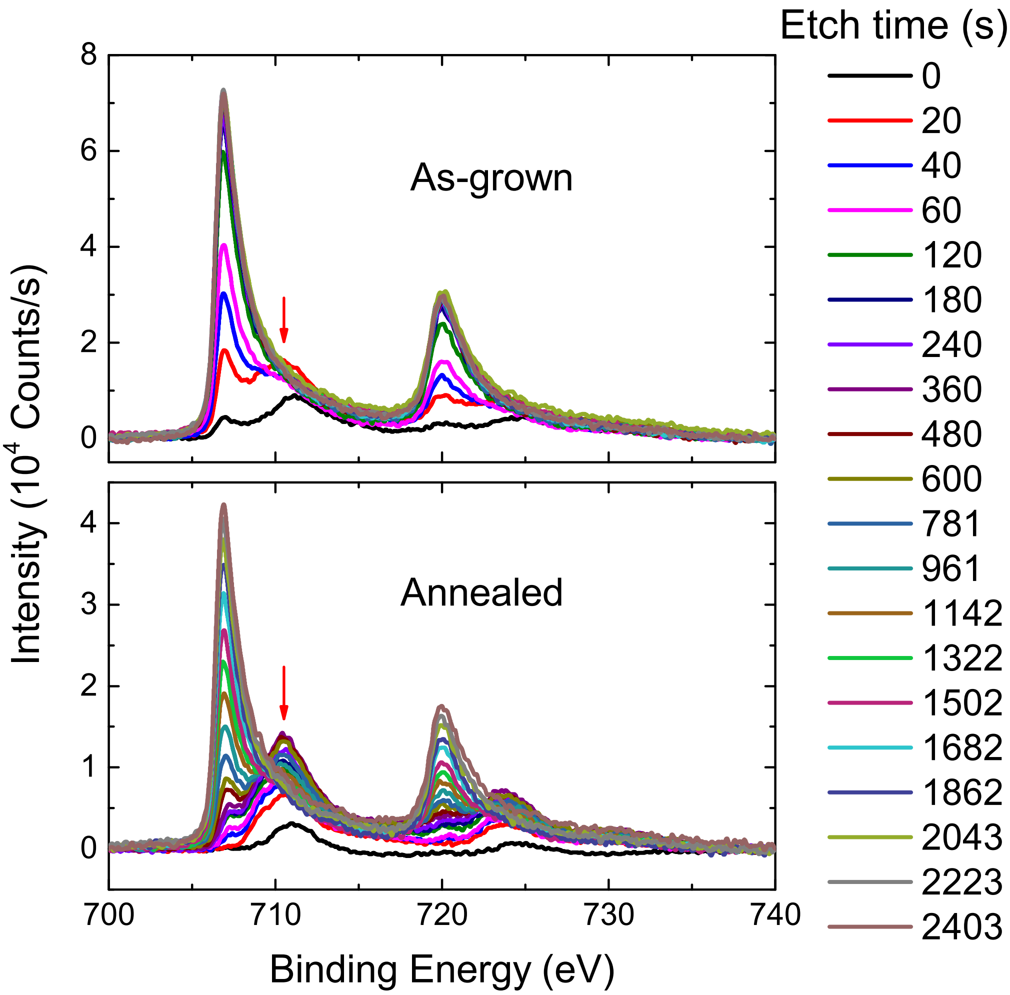

Figure S8 Raw data of the XPS spectra of Fe 2p state for the as-grown and annealed samples in a wide range of etch time. For the as-grown sample, the peak at 710.5 eV (see the red arrowed line, representing an elevation of the Fe valence) is only present for etch time in the range below 40 s. In contrast, for the annealed sample, this peak disappears only when the etch time reaches near 1000 s.

1. Ma, Y. H. *et al.* Growth and characterization of millimeter-sized single crystals of CaFeAsF. *Supercond. Sci. Technol.* **28**, 085008 (2015).