Supplementary Information for

Sol-Gel Synthesis of Zinc Ferrite-Based Xerogel Monoliths with Well-Defined Macropores

Yasuki Kido, Kazuki Nakanishi,* and Kazuyoshi Kanamori

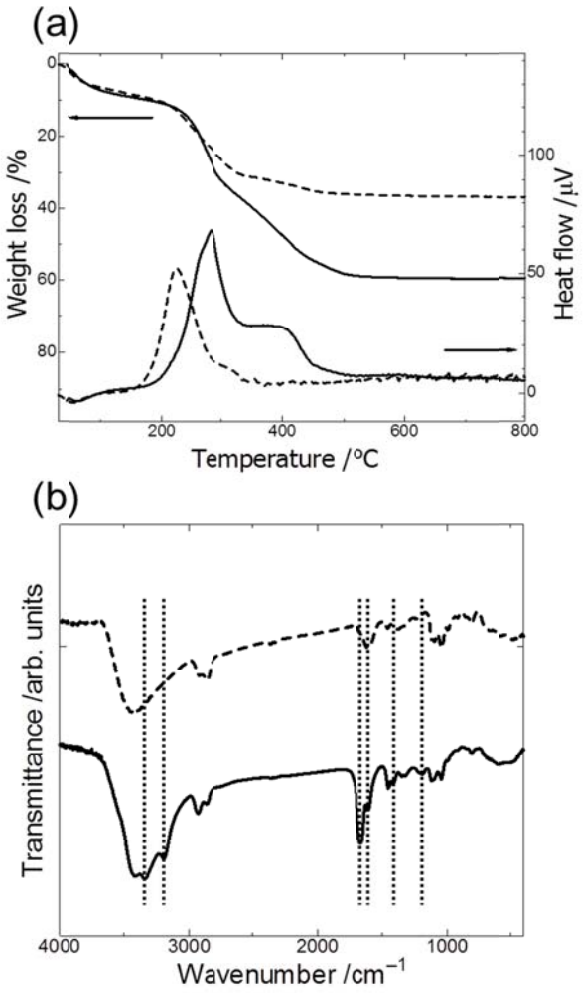

Fig. S1 (a) TG-DTA curves for gel phase of as-dried samples prepared without PAAm (dashed lines) and with PAAm (solid lines). Weight loss and exothermic peaks from 200 ºC to 300 ºC observed in both samples are ascribed to crystallization to $ZnFe_2O_4$ and decomposition of glycerol, and those from 300 ºC to 400 ºC observed in sample prepared with PAAm is the combustion of PAAm. (b) FT-IR spectra of as-dried samples prepared without PAAm (dashed line) and with PAAm (solid line). Dotted lines indicate as following bondings: C-N for 1,196 cm^{-1}, CH_2 for 1,420 cm^{-1}, N-H for 1,604 cm^{-1}, 3,196 cm^{-1}, and 3,342 cm^{-1}, and C=O for 1,664 cm^{-1}, respectively. Appearance of new bands and intensity growth derived from PAAm are observed.

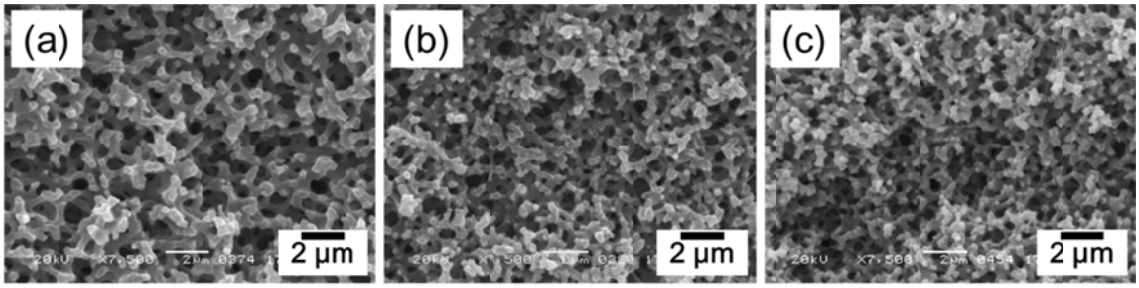

Fig. S2 SEM images of as-dried samples with varied volume ratio of V_{H2O}/V_{GLY}; (a) 1.50/2.50, (b) 1.25/2.75, and (c) 1.00/3.00, respectively. With increased the amount of glycerol, macrostructures become finer.

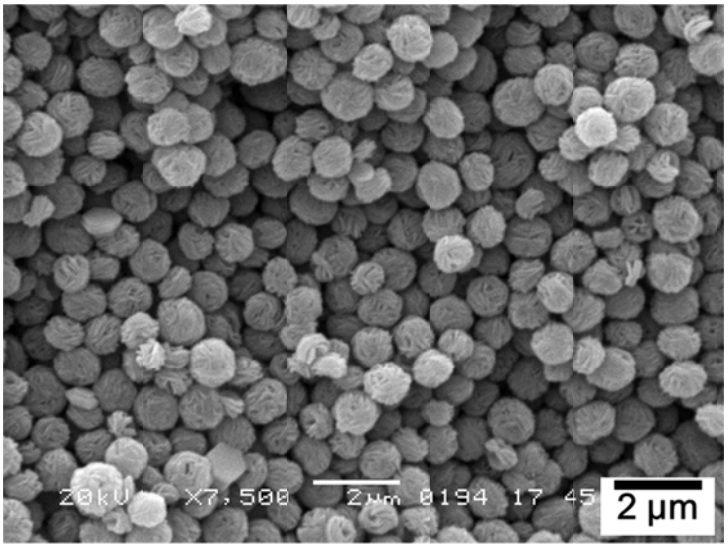

Fig. S3 SEM image of as-dried sample synthesized from only zinc chloride as a metal precursor without adding any iron(III) chloride hexahydrate. No micrometer-ranged skeleton was observed, and the aggregation of spherical particles less than 1 μm was formed.

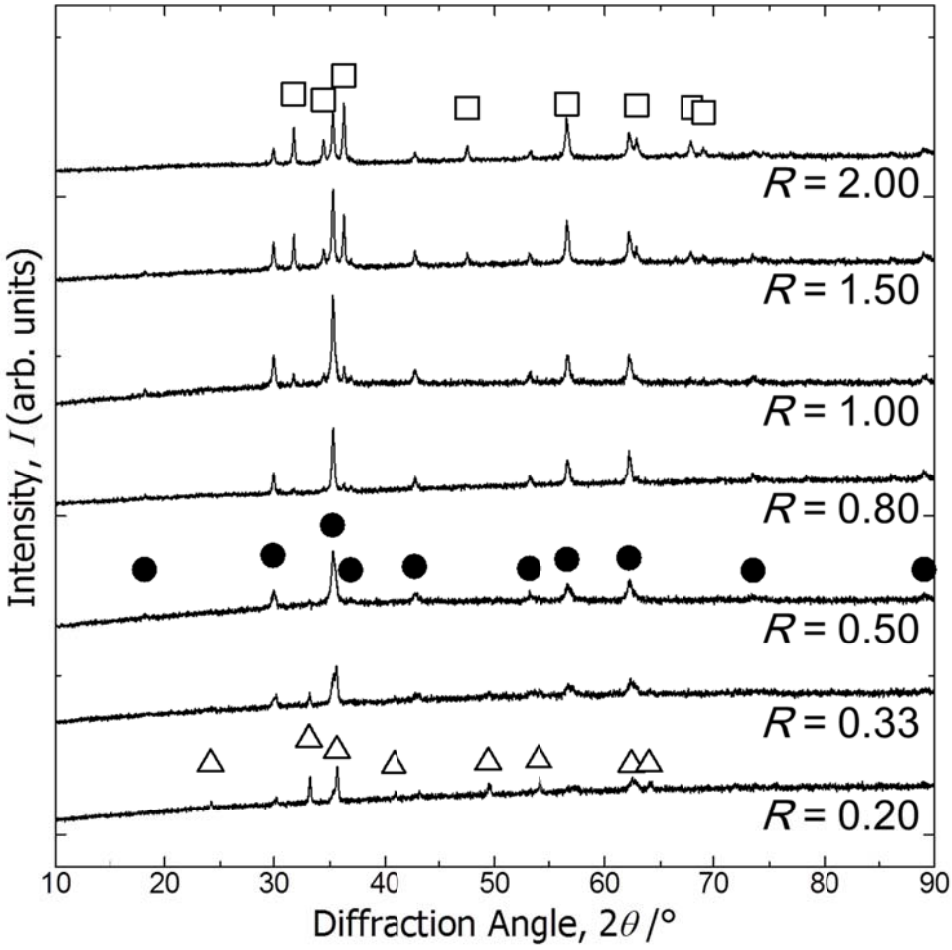

Fig. S4 XRD patterns of samples heat-treated in air at 300 ºC for 4 h with varied the ratio of Zn to Fe, *R*, from 0.20 to 2.00. Symbols indicate as follows: open triangle is α-Fe_2O_3, closed circle is $ZnFe_2O_4$, and open square is ZnO, respectively. With increasing *R*, crystalline phase changes from α-Fe_2O_3 through $ZnFe_2O_4$ to ZnO.

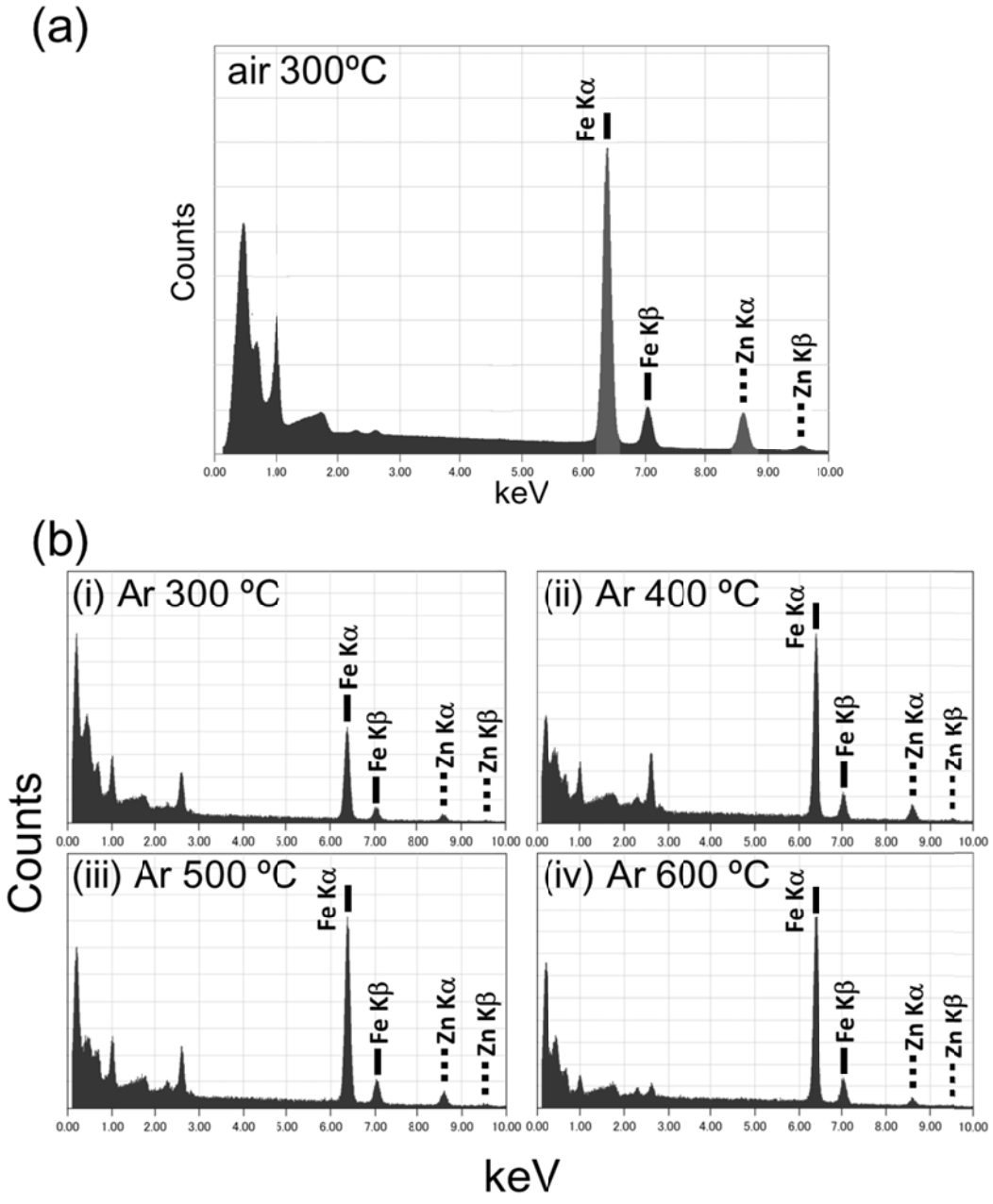

Fig. S5 EDX analysis of samples calcined under (a) air, and (b) Ar flow at different temperature.

Table S6. Caicination condition and the Zn/Fe ratio calculated from EDX analysis depicted in Fig. S5. Under air heat-treatment, Zn/Fe is close to 0.50, which is starting composition, on the other hand, Zn/Fe decreases to 0.08~0.22 under Ar heat-treatment, which results indicates there are few zinc-based species at the surface.

Calcination Condition	Zn/Fe
air 300 ºC, 4 h	0.42
Ar 300 ºC, 4 h (with continuous Ar flowing)	0.20
Ar 400 ºC, 4 h (with continuous Ar flowing)	0.22
Ar 500 ºC, 4 h (with continuous Ar flowing)	0.19
Ar 600 ºC, 4 h (with continuous Ar flowing)	0.08

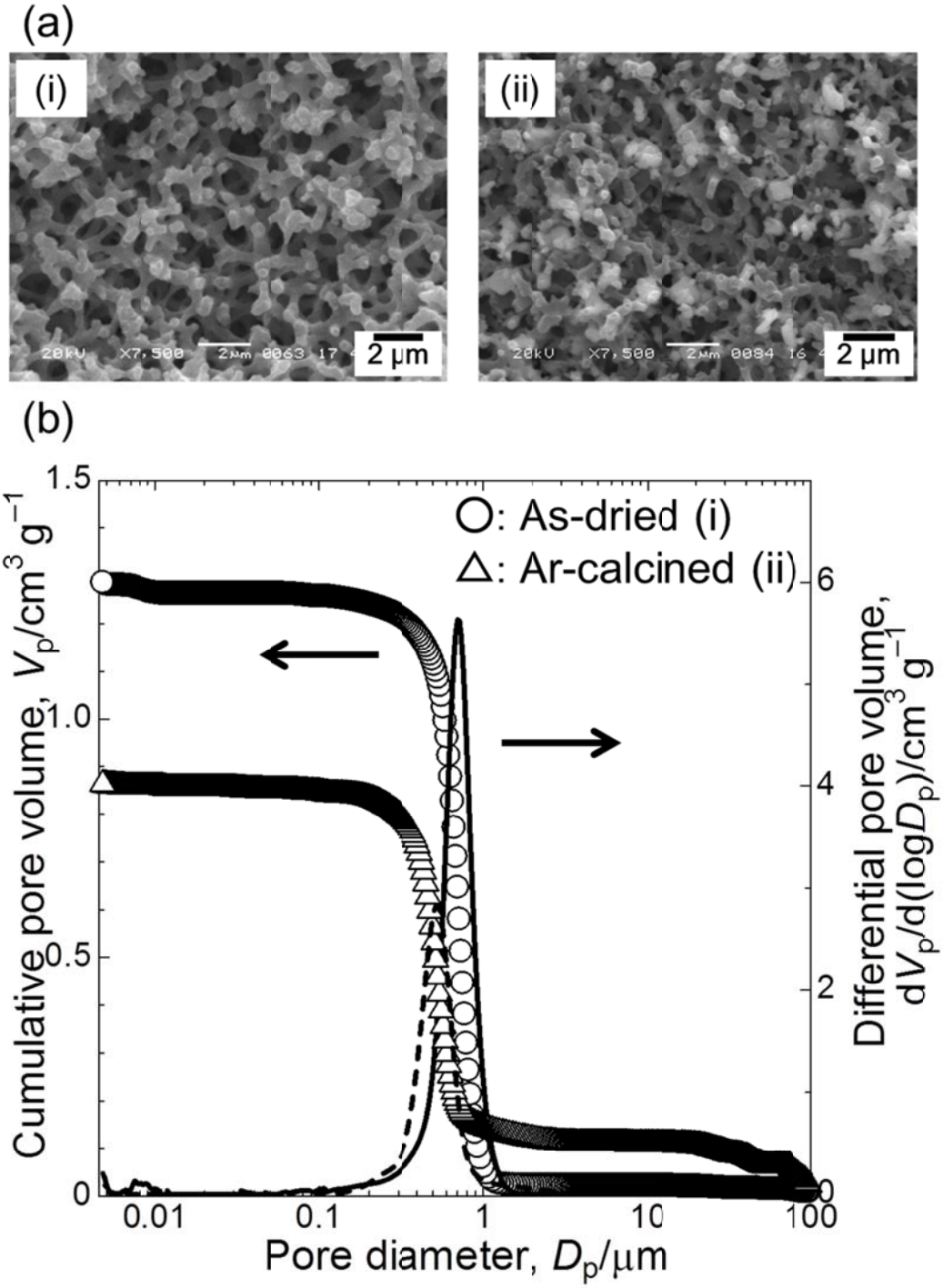

Fig. S7 (a) SEM images of (i) as-dried sample and (ii) that of heated under Ar at 600 ºC. (b) Mercury intrusion results indicate macropore size distribution and cumulative pore volume; as-dried sample (open circle, solid line) and calcined sample (open triangle, dashed line). Heat-treated sample also possessed well-defined macropore about 533 nm. Compared to as-dried sample, shrinkage of macropore as well as reduction of cumulative pore volume was observed.