Electronic Supplementary Material (ESI) for Nanoscale
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Supplementary information

Wire-in-Tube Structure Fabricated by Single Capillary Electrospinning *via* Nanoscale Kirkendall Effect: the Case of Nickel-Zinc Ferrite†

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This file contains Supplementary Figures S1 to S4 with legends.

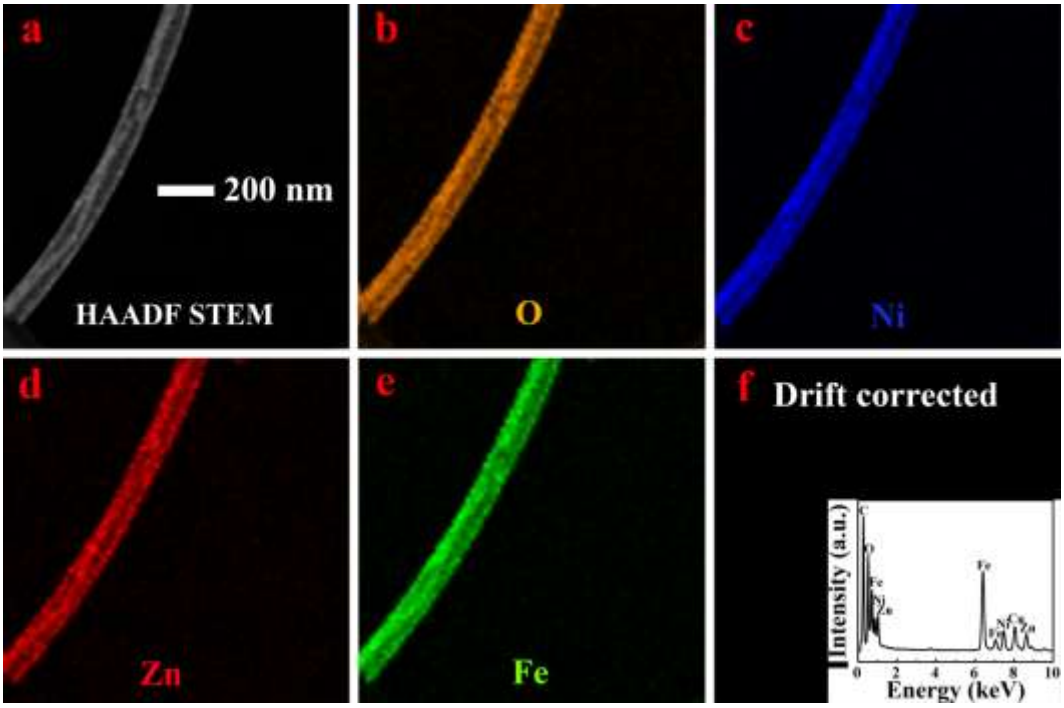

Figure S1. Elemental mappings of a single $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanowire-in-nanotube performed with a drift corrected system: (a) HAADF-STEM image; (b) oxygen element map; (c) nickel element; (d) zinc element; (e) iron element map; (f) a drift correction image, Inset, EDX spectrum collected from the a cluster of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanowire-in-nanotubes. All the scale bars are 200 nm.

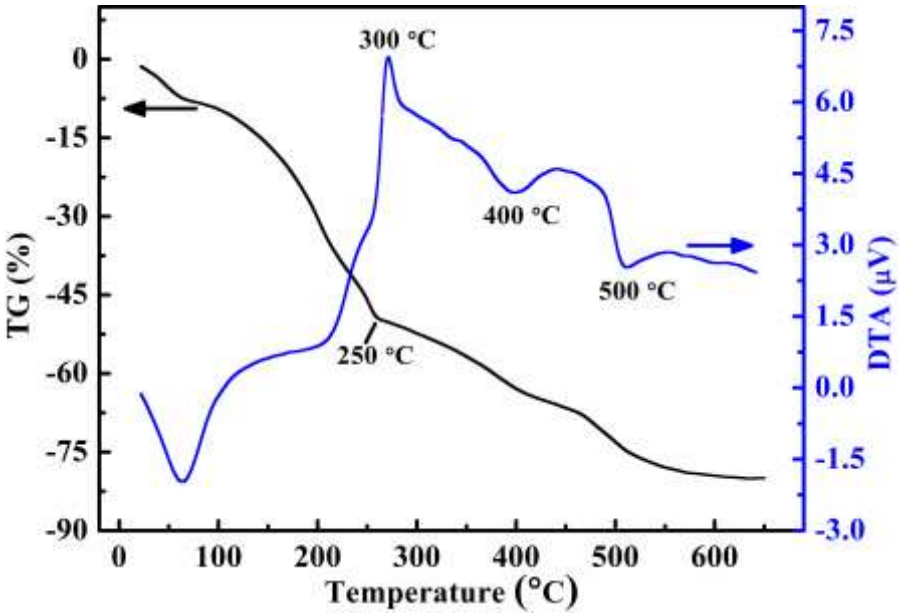

Figure S2. TG/DTA curves illustrating the transformation of the precursor nanofibres to $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanowire-in-nanotube.

To investigate the process of reactions of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanowire-in-nanotube, DTA and TG were utilized to simulate the calcination process by heating an appropriate amount of PVP/nickel nitrate/zinc nitrate/iron nitrate nonahydrate polymer composite nanofibres in an alumina crucible at 1 °C/min. The system was encased and the air re-circulated. As shown in Figure S2, the polymer composite nanofibres have four main weight loss stages in the temperature range of 50-650 °C. The first weight loss occurs at around 40-200 °C with an endothermic peak at 200 °C and is attributed to water and solvents evaporation. The second weight loss occurs at around 200-300 °C. This may be attributed to the loss of water of crystallization and the decomposition of the nitrates. The third weight loss at around 300-400 °C can be ascribed to the decomposition of the nitrates and the PVP. The fourth weight loss at around 400-500 °C is the carbon released by the decomposition of the PVP. At higher temperatures seldom weight loss is observed. Two weak broad exothermic peaks in the range of 400-650 °C are observed, those exothermic peaks can be attributed to the generation of $Ni_{0.5}Zn_{0.5}Fe_2O_4$.

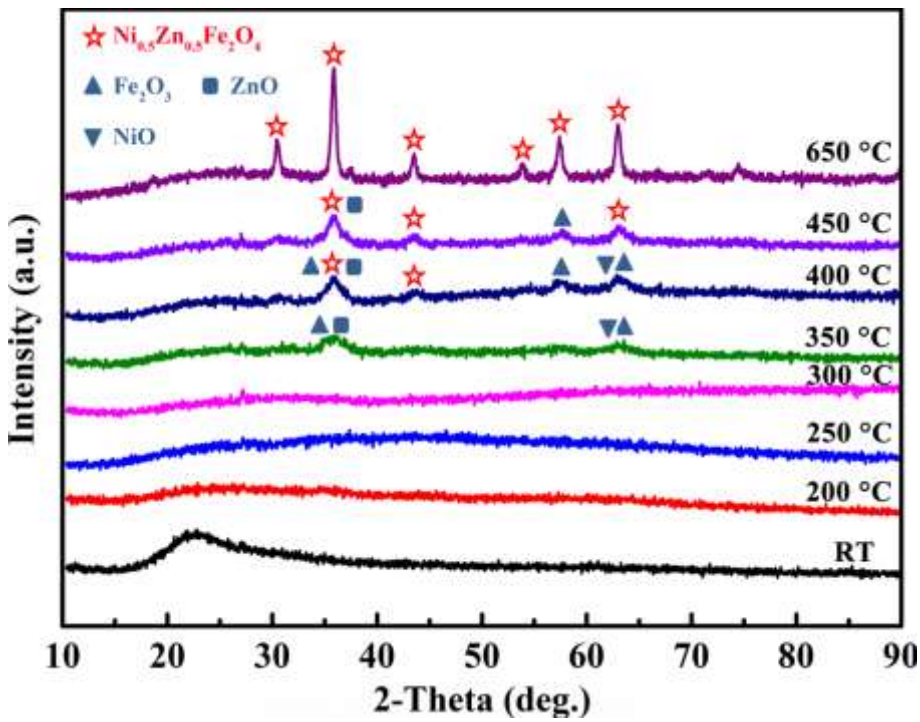

Figure S3. XRD spectrum of electrospun polymer composite nanofibres calcined at different temperature stages (room temperature, 200 °C, 250 °C, 300 °C, 350 °C, 400 °C, 450 °C, 600 °C).

To further verify the formation of $Ni_{0.5}Zn_{0.5}Fe_2O_4$, the phase transition during the calcination process of the polymer composites nanofibres was investigated using XRD techniques. Figure S3 shows the XRD patterns of polymer composites nanofibres calcined at different temperatures. The nanofibres calcined at < 300 °C exhibit a highly amorphous nature. After the nanofibres calcined at 350 °C, the crystal structure is consistent with that of Fe_2O_3, ZnO and NiO. The XRD pattern for the nanofibres heated to 400 °C clearly indicates that the burnt nanofibres are defined as Fe_2O_3, ZnO, NiO and $Ni_{0.5}Zn_{0.5}Fe_2O_4$. After calcinations at 450 °C, the major phase is $Ni_{0.5}Zn_{0.5}Fe_2O_4$, with only a small amount of residual Fe_2O_3 and ZnO. After the calcinations at 650 °C, the only phase retained is $Ni_{0.5}Zn_{0.5}Fe_2O_4$, indicating the reaction is complete. This result is in good agreement with the TG-DTA results.

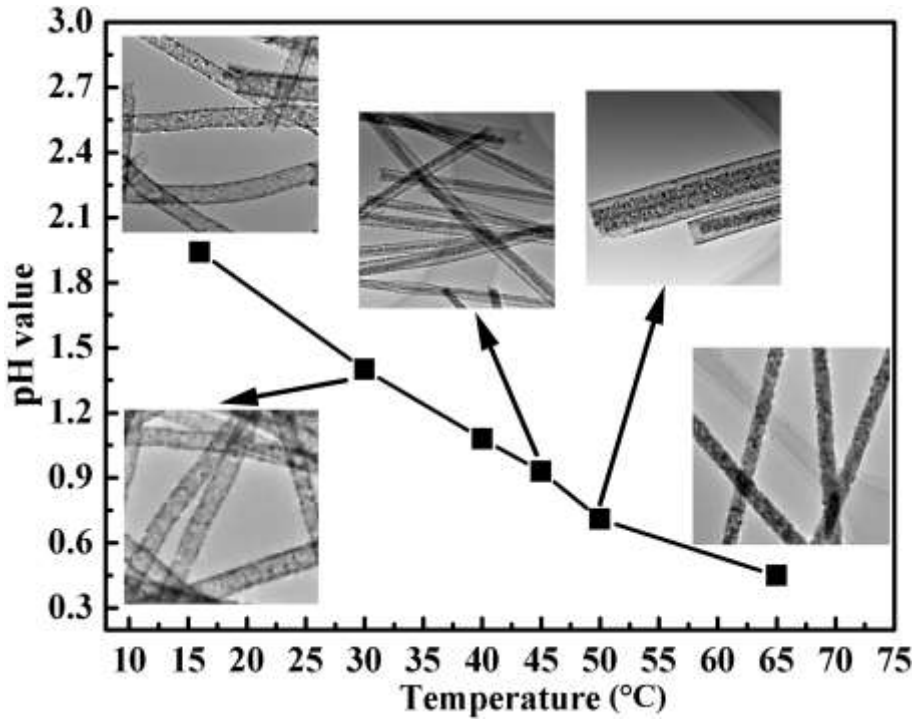

Figure S4. The temperature dependence of the extent of pH value (hydrolysis/alcoholysis), Insets show the corresponding obtained morphologies at the different temperature stages.

To further verify the formation mechanism of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanowire-in-nanotube, we have performed the investigation of morphology dependence of extend of hydrolysis/alcoholysis (*ie.* the heating temperature of heating accessory), as shown in Figure S4. It can be found that the morphology of calcined nanofibers has experienced three stages, hollow nanofibers, nanowire-in-nanotube-like nanofibers and solid nanofibers with the temperature increasing of heating accessory. Below temperature of 30 °C, the electrospinning sol-gel has few hydrolysis/alcoholysis and it cannot lead the formation of inner-wire structure. When temperature up to ~45 °C, the extend of hydrolysis/alcoholysis of nitrates was greatly increased, which leads to the formation of inner-wires. It is worth noting that the diameter of inner-wires increases with the temperature increasing, which is attributed to the enough hydrolysis/alcoholysis products diffusing to the core-region of nanofibers. With the temperature increasing further, the

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hydrolysis/alcoholysis products was highly increased, which leads to the bigger diameter of inner-wires. A direct evidence is that the calcined nanofibers show solid nature.