Metal catalyst for low-temperature growth of controlled zinc oxide nanowires on arbitrary substrates

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We have demonstrated the generation of piezoelectric power from ZnO nanowires grown on naturally oxidised silver coated on a flexible poly(dimethylsiloxane) (PDMS) substrate using the low-temperature aqueous hydrothermal growth method. A PDMS substrate was prepared using Sylgard 184A and B (Dow Corning) mixed at a 10:1 mass ratio. The PDMS substrate was then cured at 85 °C for 25 hours. Figure S1a shows an SEM image of ZnO nanowires grown on oxidised silver nanoparticles on a flexible PDMS substrate. The Ag nanoparticles were synthesised using the chemical reduction of silver nitrate in ethanol solution and were then oxidised in ambient air. Because the surface of the Ag nanoparticle layer was very rough, the nanowires grew in random directions. Due to the flexibility of the PDMS substrate, the sample easily bends, as shown in Fig. S1b. The flexibility of ZnO nanowire-coated PDMS contributes to the generation of piezoelectric energy, as demonstrated in Fig. S1d. As shown in Fig. S1c, PMMA was spin-coated to insulate two electrodes on both sides of the ZnO nanowires. To complete the device, a 1.5×4 cm^2 Ag layer was deposited onto the open top of the ZnO

nanowires by RF sputtering. The two electrodes were coupled with a HP 34401A multimeter and a data acquisition system with a Labview-based interface. Figure S1d demonstrates that the increase in the output voltage is correlated with the bending. When the sample was bent, the maximum voltage was 100 μV. When the sample was released, the maximum voltage was between -200 and approximately -400 μV. These piezoelectric voltages are attributed to the internal stress, which suggests that the vibration of this material can lead to nanowire expansion and compression.

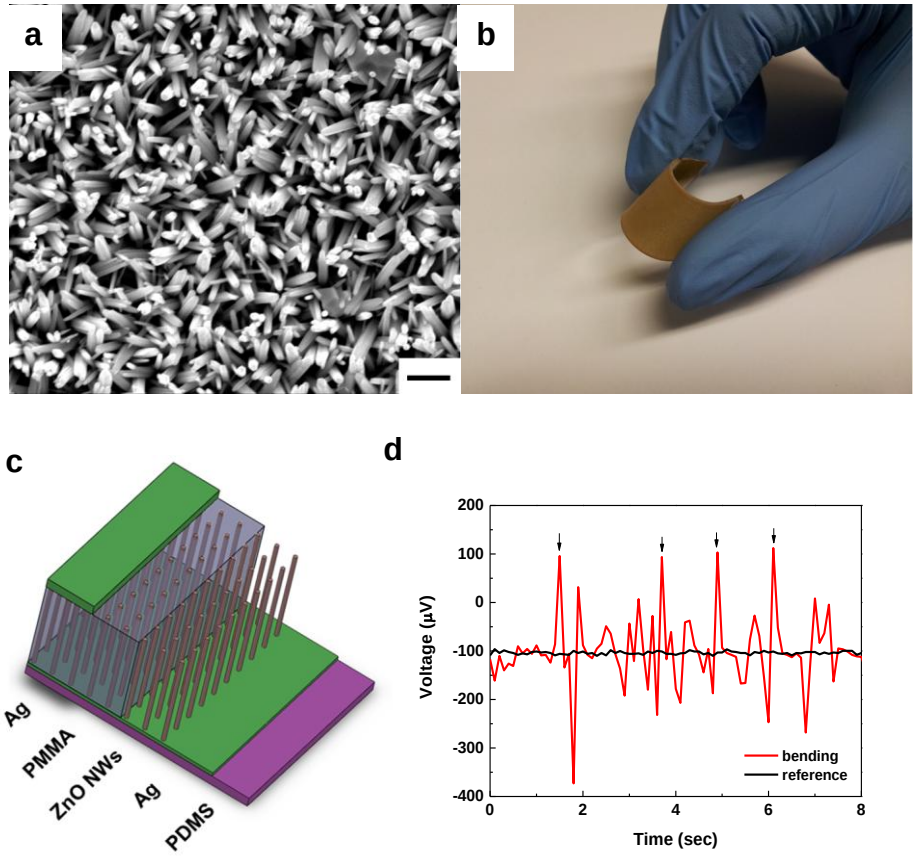

Figure S1 | Generation of piezoelectric power from ZnO nanowires grown on a flexible substrate. a, SEM image (scale bar = 1 μm) and **b**, picture of ZnO nanowires grown on a PDMS substrate. The concentration of a nutrition solution was 20 mM, and the initial pH values were 9~9.5. **c**, Schematic diagram of the device. **d**, Voltage characteristics of ZnO nanowires as a function of time. Arrows indicate when the device was bent.

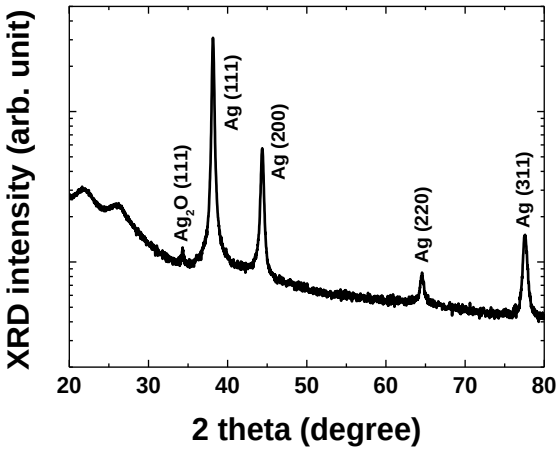

Figure S2 | XRD analysis of naturally oxidised silver deposited on polyimide by RF sputtering.

Figure S2 presents XRD data of a naturally oxidised silver film on a polyimide substrate. The peak position at 34.32° is related to Ag_2O (111), corresponding to the XRD peak position of ZnO (002).

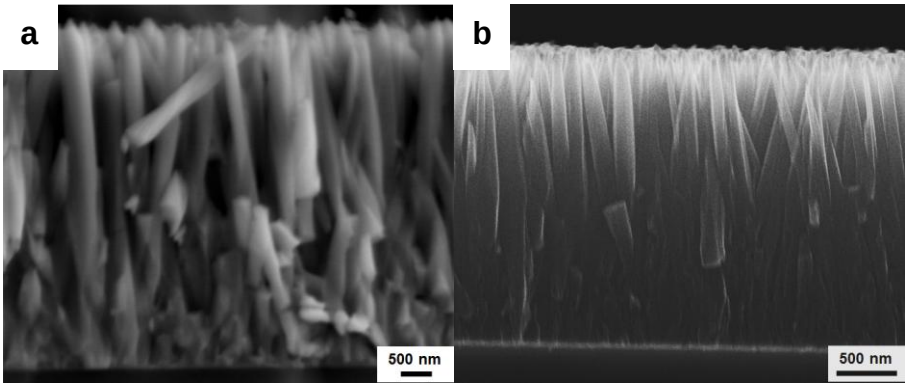

Figure S3 | Similar structural properties of ZnO nanowires grown on different seed layers. SEM images of ZnO nanowires on (a) 20 nm-thick ZnO film on silicon substrate and (b) 50 nm-thick Ag layer on polyimide film. Scale bars are 500 nm.

To compare ZnO nanowires grown on differerent seed layers, we have taken more SEM images of ZnO nanowires on a thin ZnO film and a thin Ag film, as shown in Fig. S3. Although ZnO nanowires were heterogeneously grown on oxidized Ag layers, the ZnO nanowires are similar in structural properties of ZnO nanowires grown on a perfectly lattice-matched ZnO seed layer. These results explicit that ZnO nanowires can grow vertically on an oxidized Ag layer.

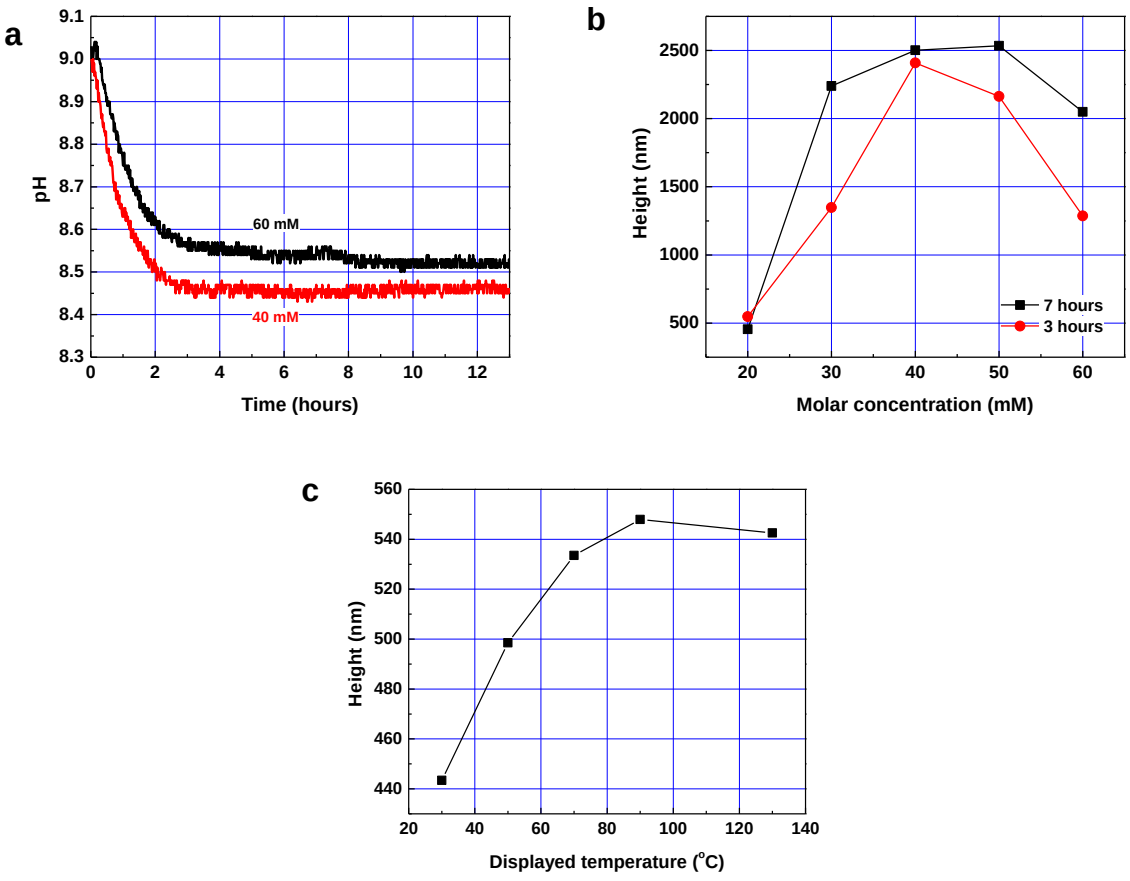

Figure S4 | Various growth conditions of ZnO nanowires. a, In situ pH and solution temperature as functions of reaction time and molar concentration at a set temperature of 90 °C. **b**, Average heights of ZnO nanowires as a function of molar concentration at a set temperature of 90 °C. The reaction times were 3 hours and 7 hours. **c**, Average heights of ZnO nanowires as a function of displayed temperature. The reaction time and molar concentration were 3 hours and 20 mM, respectively. All average heights of ZnO nanowires were measured from cross-sectional SEM images.

Due to the increased concentrations of the nutrition solutions with pH values greater than 8.4 (Fig. S4a) and the increased amount of Zn^{+} ions, these ZnO nanowires grew much longer than those synthesised in the 20 mM nutrition solution, as shown in Fig. S4b. However, the ZnO nanowires continuously grew to ~2.500 μm in the 40 mM nutrition solution, whereas, in nutrition solutions with concentration greater than 40 mM, the ZnO nanowires were dissolute in solution. As the solution temperature was increased to 90 °C, the height of the ZnO nanowires increased (Fig. S4c). The height of the ZnO nanowires reached a plateau at solution temperatures greater than 90 °C because the increased Zn^{+} ions due to the enhanced ion dissociate rate at high temperature contributed to the growth of lateral planes of the ZnO nanowires.

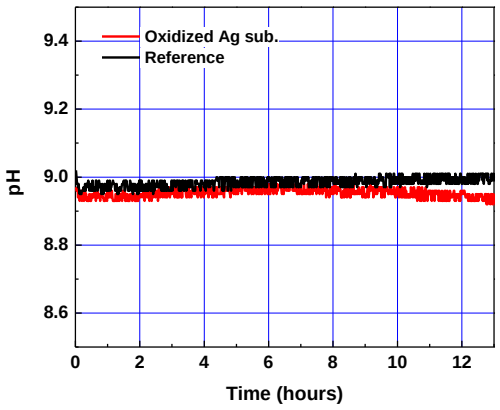

Figure S5 | pH values of a solution with oxidised silver films on polyimide and a reference solution at room temperature. All solutions were prepared at 20 mM.

Figure S6a shows an SEM image of the ZnO nanostructures after 10 min in a 20 mM solution. These ZnO nanostructures grew like islands and the growth depends on the growth rates of different growth planes in the ZnO crystals and on the short mean free paths of ions due to the low solution temperature; this dependence is due to the growth occurring according to the

Volmer–Weber mechanism (i.e., island growth mode) rather than the Frank–Merwe mode (layer-by-layer growth mode) to reduce the strain during growth. At 15 min, ZnO nanostructures partially covered the silver surface, as shown in Fig. S6b. Figure S6c shows the ZnO nanowires fully grown on the silver substrate after 30 min.

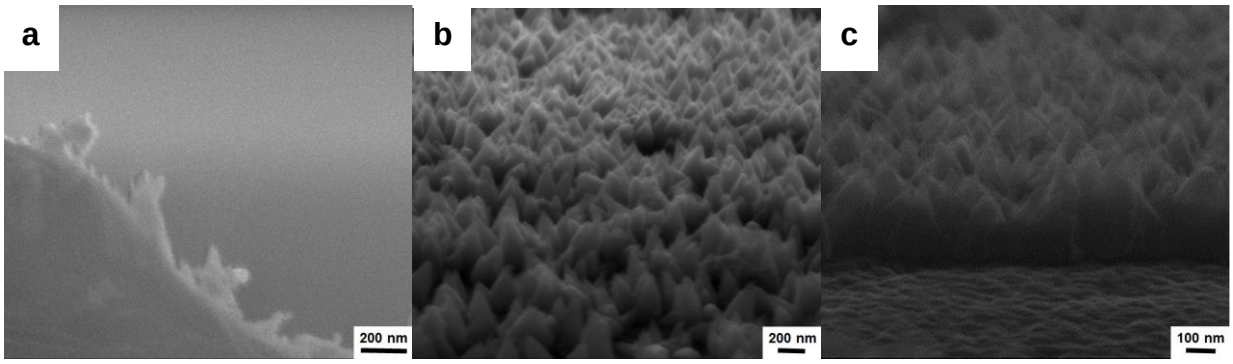

Figure S6 | Growth steps of ZnO nanowires. SEM images of ZnO nanostructures grown on oxidised silver for (a) 10 min, (b) 15 min, and (c) 30 min, respectively.

Basically, the ZnO nucleation occurs at stable sites with lowest surface energy. The sites with large lattice mismatch between ZnO and metal substrate are forced to separate ZnO nucleus due to their high surface energy [1]. To reduce surface energy and lattice mismatch, water molecules can oxidize the ionized metal layer using environmental thermal energy given by $M^{+}+ OH^{-} \rightarrow M(OH) \rightarrow MO^{-} + H^{+}$, where M is metal. Usually, ionized metal atoms result from oxidized metal atoms, which have been exposed and oxidized in ambient air. These oxidation processes on metal surfaces are used to happen non-uniformly. In addition, the lattice constant of a metal oxide layer seriously affects the growth of ZnO nanostructures on itself. Therefore, when the both requirements are met, ZnO nanowires can be successfully grown on the metal oxide

layer. Figure S7 illustrates the growth mechanism of ZnO nanoflowers on the oxidized metal layer. Whereas non-uniformly localized metal oxide sites collect ZnO nucleus and grow ZnO nanowires along with the morphology of ZnO nucleus, Ag^{+} ions can oxidize metal surface very uniformly and metal atoms are negatively ionized easily to meet Zn^{2+} ions when Ag^{+} ions are detached. Once ZnO islands are formed, ZnO nanowires are grown further on those islands following c-plane of ZnO.

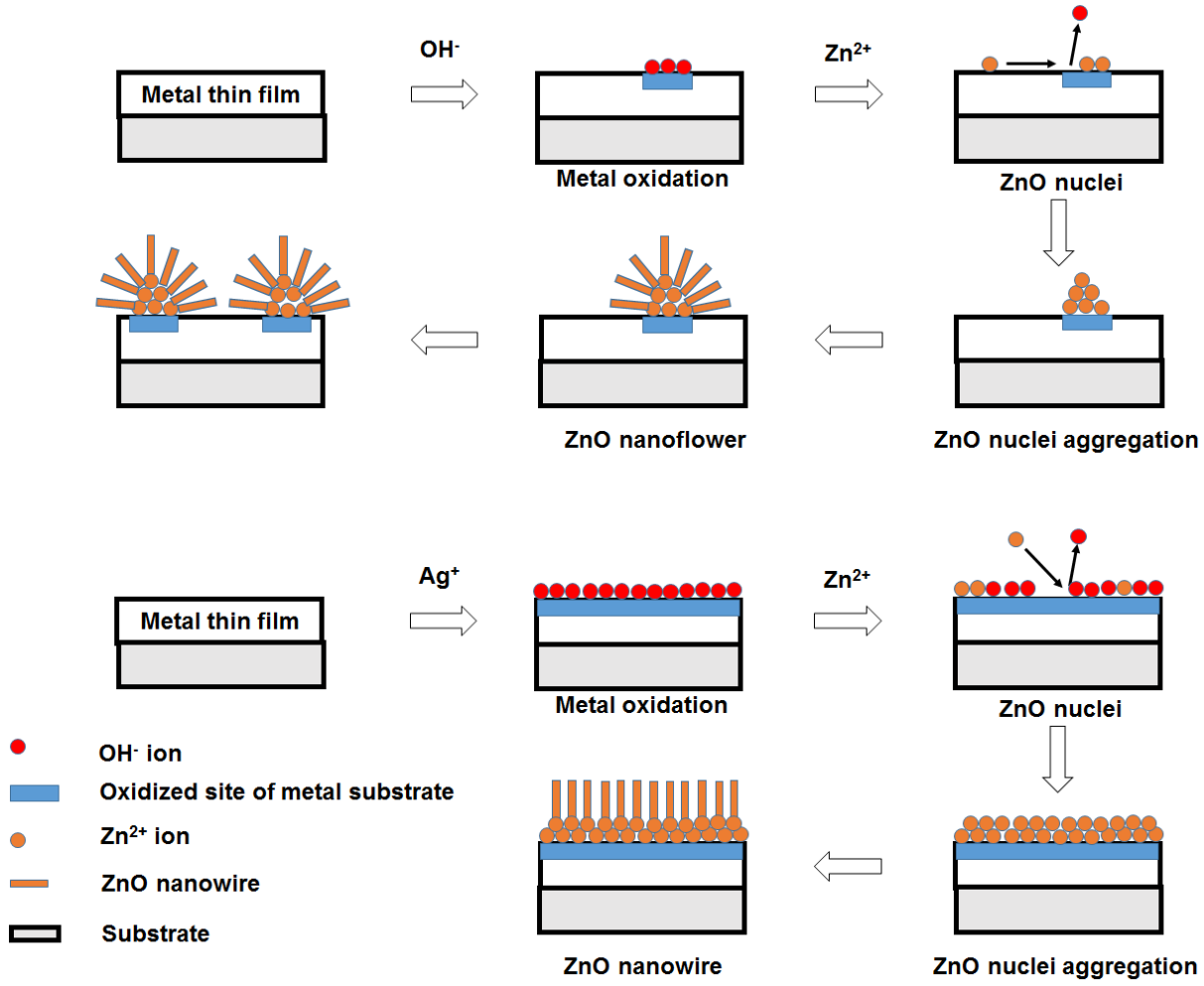

Figure S7 | Growth mechanism of ZnO nanoflowers and nanowires on a metal layer.

We applied silver nitrate to a copper film deposited by RF sputtering on a polyimide substrate. Normally, ZnO nanowires do not grow on Cu substrates because $Cu(OH)_2$ is soluble in the ammonia solution used to increase the pH. However, when 1 mM silver nitrate was added to the nutrition solution, ZnO nanowires were successfully grown, as shown in Fig. S8. During the growth of the ZnO nanowires, Ag particles self-synthesised and stacked on the ZnO nanowires. These particles were confirmed to be Ag particles by EDS analysis.

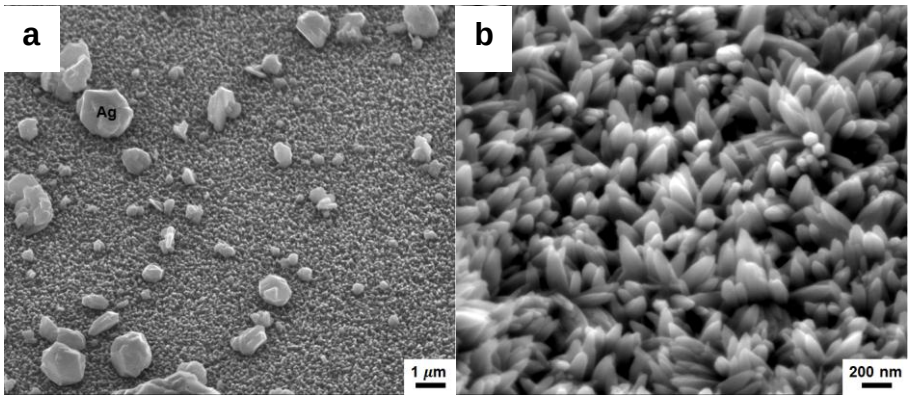

Figure S8 | Growth of ZnO nanowires on copper substrates. (a) low- and (b) high-magnification SEM images of ZnO nanowires on copper substrates deposited on polyimide using RF sputtering. Silver nitrate (1 mM) was added to the 40 mM nutrition solutions.

Reference

[1] Shi, R., Yang, P., Zhang, S., and Dong, X. Growth of flower-like ZnO on polyhedron CuO fabricated by a facile hydrothermal method on Cu substrate. *Ceram. Int.* **40**, 3637-3646 (2014).