Harvesting Mechanical and Thermal Energy by Combining ZnO Nanowires and NiTi Shape Memory Alloy

Harry Radousky[1,3], Fang Qian[1], Yonghao An[1], Zhidan Zeng[1], Gongming Wang[2], Yat Li[2], Luman Qu[1,3], Gergely Zemanyi[3], and Y. Morris Wang[1]

[1.] Materials Science Division, Lawrence Livermore National Laboratory;
[2.] Chemistry and Biochemistry Department, UC-Santa Cruz;
[3.] Department of Physics, UC Davis (radousky1@llnl.gov)

Abstract:

In the expanding world of small scale energy harvesting, the ability to combine thermal and mechanical harvesting is growing ever more important. We have demonstrated the feasibility of using ZnO nanowires to harvest both mechanical and low-quality thermal energy in simple, scalable devices. These devices were fabricated on kapton films and used ZnO nanowires with the same growth direction to assure alignment of the piezoelectric potentials of all of the wires. Mechanical harvesting from these devices was demonstrated using a periodic application of force, modeling the motion of the human body. Tapping the device from the top of the device with a wood stick, for example yielded an Open Circuit Voltage (OCV) of 0.2 - 4 V, which is in an ideal range for device applications. To demonstrate thermal harvesting from low quality heat sources, a commercially available Nitinol (Ni-Ti alloy) foil was attached to the nanowire piezoelectric device to create a compound thermoelectric. When bent at room temperature and then heated to 50ºC, the Nitinol foil was restored to its original flat shape, which yielded an output voltage of nearly 1 V from the ZnO nanowire device.

Keywords: nanowires, compound thermoelectrics, mechanical energy harvesting

1. Introduction

A tremendous about of work has been done recently to improve energy harvesting capabilities from mechanical and thermal sources by using nanomaterials [1]. For example, a number of advances have been made in pure thermoelectric materials using hierarchical nanostructures [2-3] and vacancy-induced dislocations [4] as well in flexible devices for piezoelectric harvesting [5]. In this paper, we have investigated the feasibility of using ZnO nanowires to harvest both mechanical and low-quality thermal energy. ZnO nanowires have been used extensively for energy harvesting, utilizing both its thermoelectric and piezoelectric properties [6-7].

Mechanical harvesting of the energy from human motion has the potential to power many of the small devices we now carry with us.[8-9] While battery technology has made amazing advances over the past decade, there is always the need for the continuous energy replacement made possible from harvesting mechanical vibration. At the same time, the world is full of heat sources to harvest using thermoelectric generators (TEGs). Most thermoelectrics have high efficiency, i.e., have a reasonable figure of merit only for relatively high temperatures of 300^{o}C or greater. Harvesting from a low quality heat source (defined as less than 100^{o}C) such as computers, hot asphalt, cars left in the sun, etc., is not efficient for current thermoelectric materials. For example, running a temperature measurement program on your computers CPU would show temperatures in the range of 40-60^{o}C, depending on what tasks you are asking the CPU to perform. In this work, we utilized the piezoelectric properties of ZnO to create a nanowire based device which can recover mechanical energy from human motion, and can also be used for thermal harvesting from the type of low quality heat sources mentioned by combining the ZnO nanowire device with the shape memory alloy NiTi, known as Nitinol, to create a compound thermoelectric [10-11].

2. Material and methods

We discuss below the preparation and characterization of the ZnO nanowires, followed by a description of the circuit design for our devices.

2.1. Materials

ZnO nanowires were grown using a chemical vapor deposition method. A very good review of ZnO growth and properties is given by Z. L. Wang [12]. ZnO nanowires were synthesized on a c-plane sapphire substrate in a home built tube furnace using a mixture of ZnO and graphite powders (weight ratio 1:1) as a precursor. The source material was loaded onto a mica substrate, which was placed upstream of the sapphire substrate. The quartz tube was pumped down to 100 Torr and then refilled with nitrogen gas until it reached atmospheric pressure. ZnO nanowires were grown at 1000ºC for 30 minutes. The sapphire substrate was covered with a white ZnO nanowire film.

The ZnO nanowires were of good quality, in that they were dense and uniform, with a length of 10-50 um, diameter of ~200 nm, and growth direction along the c-axis. Images for the nanowires are shown in Figure 1, panels a-c [13-14]. Measurements of the internal resistance of the wires was found to be high, which necessitated measuring the open circuit voltage (OCV) rather than a direct output power. The same growth direction of nanowires guarantees the alignment of the piezoelectric potentials of all of the wires. This alignment is illustrated in Figure 1, panels e-f. The nanowires were transferred to the Kapton substrate shown in Figure 1 by dry transfer, as shown in Figure 1d.

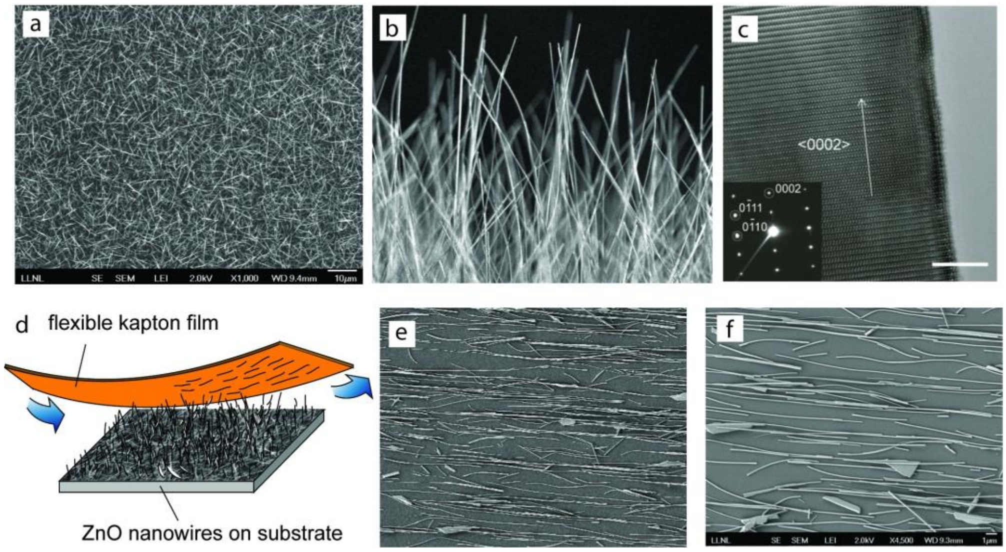

Figure 1. Growth of ZnO nanowires

2.2. Methods

The circuit shown in Figure 2 was designed as long, parallel electrode arrays perpendicular to the nanowire axis. Good-alignment of the nanowires in this configuration would enable scale-up of the output. Figure 2a shows the lithographic process used to create the energy harvesting device. Nanowires were transferred to a flexible Kapton thin film as by gentle scratching. This method yielded well-aligned nanowires on the receiving substrate as illustrated in Figure 1, panels c-e. Following dry-transfer, the Kapton film was evaporated with patterned gold electrodes using microfabrication techniques. The fabrication steps involved dry transfer of the ZnO nanowires, spin coating down the photoresist, photolithography, metal deposition and finally a lift off step.

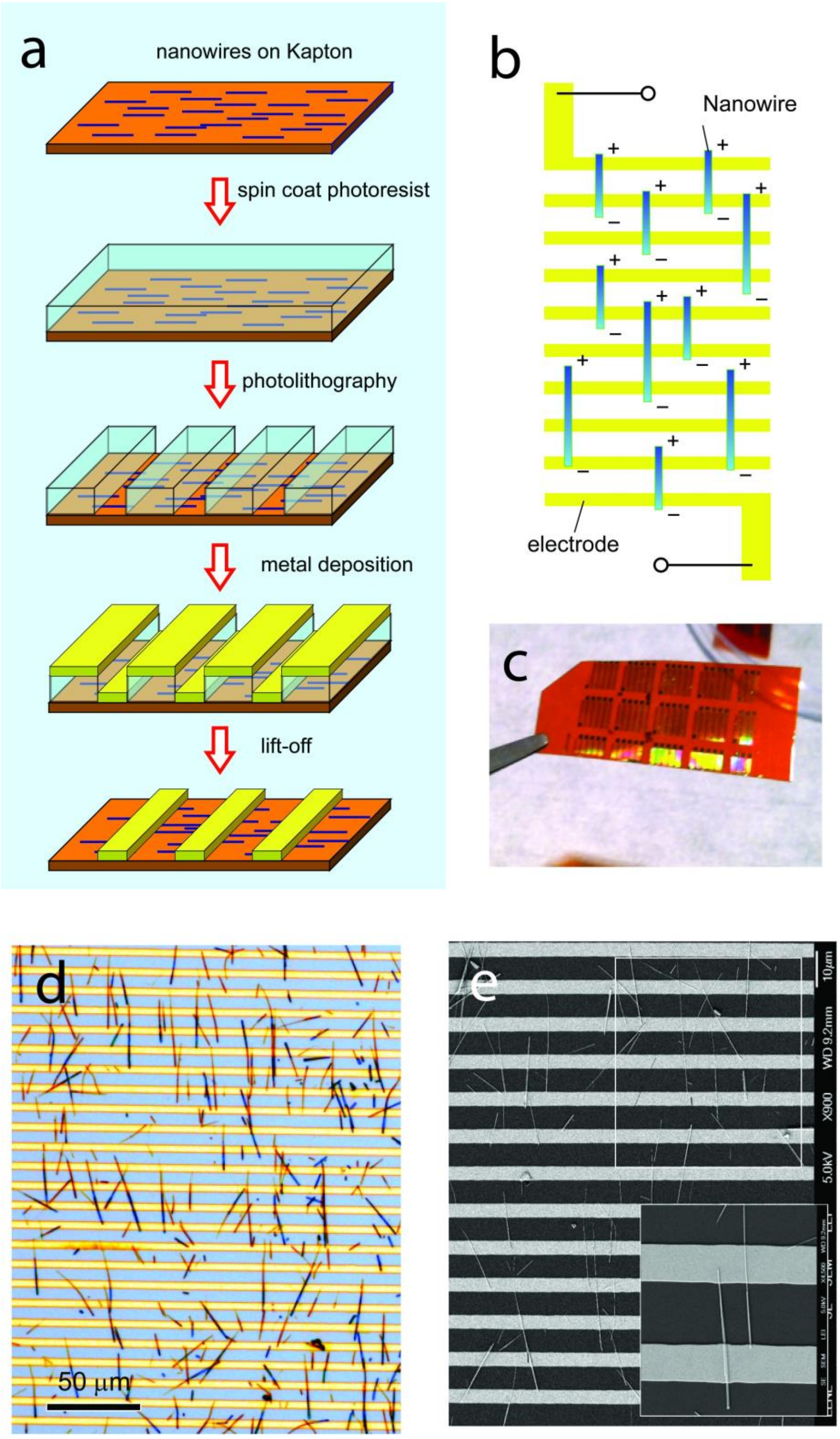

Figure 2. ZnO device design and fabrication

Ideally, the total output voltage is the sum of the voltage from individual wires in the vertical direction because they are connected in series, as shown in Figure 2b. The total output current scales up with the number of nanowires within each row of electrode pairs. There is however, an optimal number of wires for maximizing the voltage output, which is due to a balance between the increased output from placing more wires in the device, and the increased resistance to bending which results from the strength of the additional wires. This point is discussed more fully below in the section on device modeling.

3. Results and Discussion

Results were obtained both for mechanical harvesting, using the ZnO nanowire device to directly convert mechanical energy to electrical energy, and also for thermal harvesting of low quality heat by using the nanowire device coupled to a phase change material to create a compound thermoelectric as discussed below. Turning first to the mechanical harvesting, this was demonstrated using a periodic application of force as shown in Figure 3.

Our goal was to apply motions which mimic those from human motion. Tapping the device from the top with a wood stick yielded an open circuit voltage (OCV) of 0.2 - 4 V, according to the strength of the tap stimulus. These results are shown in Figure 3, panels a-d. When the bending curvature is qualitatively increased, this yielded an enhanced voltage. This is shown in Figure 3, panels e-f.

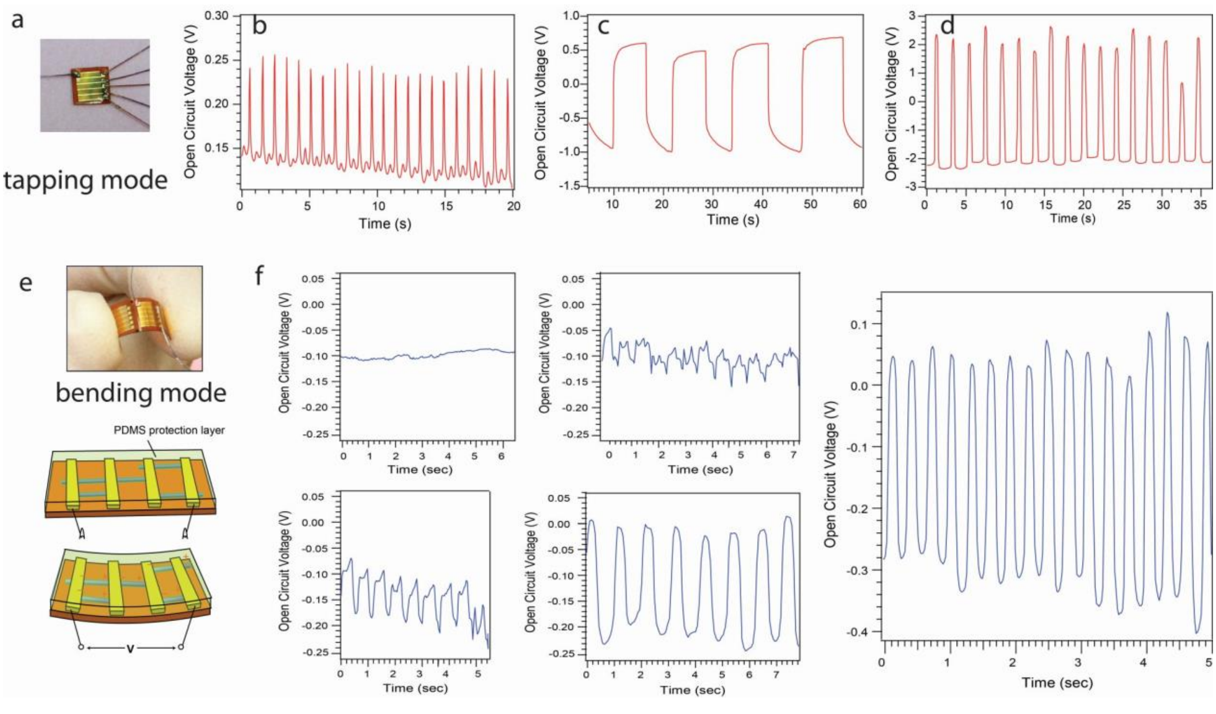

Figure 3. Mechanical harvesting results

To demonstrate thermal harvesting from low quality heat sources, a commercially available Nitinol (Ni-Ti alloy) foil, which is a well known phase transition material with transition temperature of ~ 50°C, was attached to the nanowire piezoelectric device. The whole device assembly was bent at room temperature as shown in Figure 4. Upon heating above 50°C, the Nitinol shape memory alloy underwent a structural phase transition, and was restored to its original flat shape, as shown in Figure 4a. Accordingly, the nanowire device had a drastic shape change, which yielded an output voltage/power of nearly 1 V. From the graph in Figure 4b one can see that the voltage output occurred over a range of approximately 4 seconds. This time constant results from our experimental configuration and is not a limit on the ultimate cycle time attainable in devices which are cycling between hot and cold temperature sinks.

We have conducted simple modeling of the mechanical behavior of the ZnO nanowire device using COMSOL Multiphysics. This was done by applying a force in the model which causes bending on the ZnO nanowires, which also cause tension at the point of the bend. This tension is what causes the piezoelectric voltage [15]. The COMSOL Multiphysics simulator is used to build an array of ZnO or PZT nanowires (0.2 micron in diameter * 10 micron in length) lying on a Kapton HN film back plate (110*100*125 microns) and embedded in metallic gold strips (5*100*1 microns). The boundary condition is that both ends of the back plates are fixed, and a uniform pressure of 10^5 Pa is applied on the center metallic strip. The applied force causes the back plate and nanowire array to bend together. The COMSOL solid mechanics module is used to model the bending of the components. The coupled constitutive equations for the linear piezoelectric effect of the sample system is modeled according to:

$$\sigma_{ij} = C_{ijk}\varepsilon_{kl} - e_{kji}E_k$$
$$D_i = e_{ijk}\varepsilon_{jk} + \kappa_0\kappa_{ij}E_j$$

where σ_{ij} is the stress, D_i is the electric displacement, C_{ijk} is the elastic stiffness tensor, e_{kji} is the piezoelectric strain tensor, κ_{ij} is the relative dielectric tensor (κ_0 is the vacuum permittivity). Furthermore, ε_{jk} is the strain tensor and E_k is the electric field vector. Tables 1 and 2 shows the physical properties for ZnO and PZT used in the simulation.

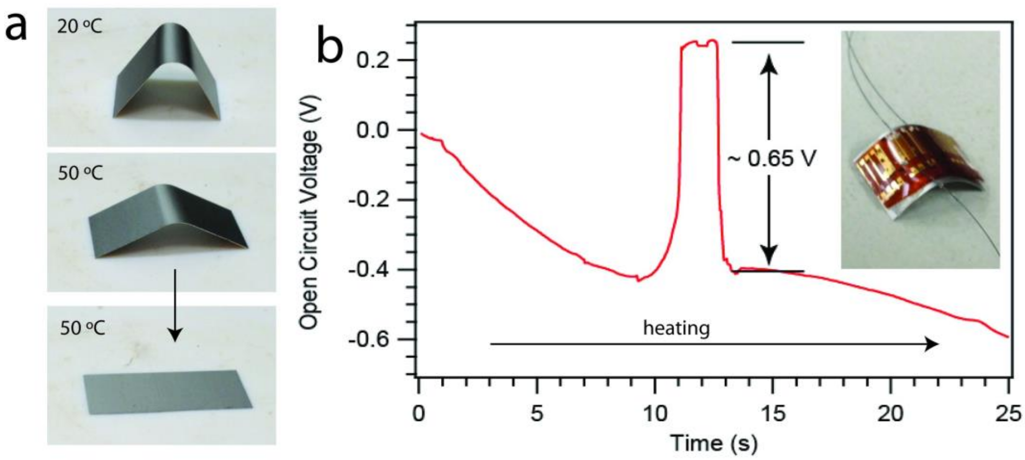

Figure 4. Thermal harvesting results

Table 1 - ZnO material properties in Voigt notation

Tensor components	11 = 22	12	13 = 23	33	44 = 55
Elastic moduli C_{ij} [GPa]	209.7	121.1	105.1	210.9	42.5
Relative electric permittivity κ_{ij}	7.77			8.91	
Tensor components			31 = 32	33	15 = 24
Piezoelectric constants e_{ij} [C/ m^2]			-0.51	1.22	-0.45

Table 2 - PZT material properties in Voigt notation

Tensor components	11 = 22	12	13 = 23	33	44 = 55
Elastic moduli C_{ij} [GPa]	138	78	74	115	26
Relative electric permittivity κ_{ij}	762.5			663.2	
Tensor components			31 = 32	33	15 = 24
Piezoelectric constants e_{ij} [C/ m^2]			-5.2	15.1	12.7

The nanowire array in the model exhibits a piezoelectric effect, generating a voltage difference across the ends. We have used the standard mechanical and piezoelectric values in the model [16]. The COMSOL electrostatics module is used in conjunction with the solid mechanics module to create the simulation and model the piezoelectric voltage difference. Grounding the Au strip on one end, the voltage of the strip on the other end of the plate is calculated. The analysis with same setup and boundary conditions is repeated for several different nanowire densities for ZnO. We have also used the same model to calculate the voltages if PZT nanowires replace the ZnO. Results from the voltages as a function of the number of nanowires in the device are shown in Figure 5 for ZnO and for PZT.

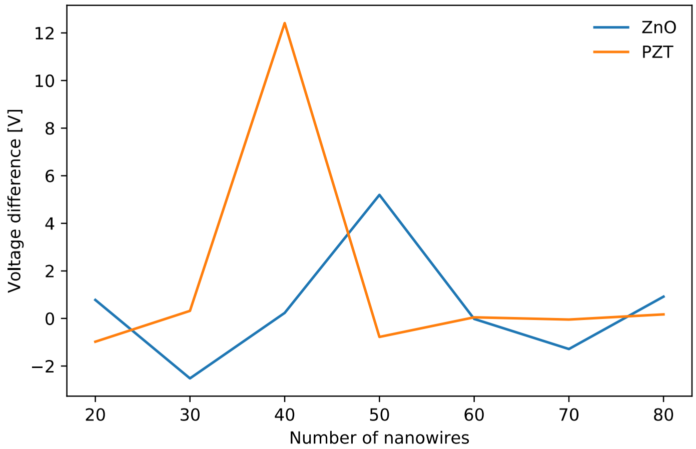

Figure 5. COMSOL simulation of voltage vs number of nanowires in the device

The key result of the modeling shows that the voltage expected is strongly dependent on the number of nanowires used per unit area. While increasing the number of nanowires should increase the total voltage, this is balanced by the strain being reduced by the added reduction in the bending achieved for the same applied force. The negative voltages seen in Figure 5 result from the coupled nature of the many nanowires, which undergo different stresses. These competing effects lead to a maximum in output voltage for approximately 50 nanowires in ZnO for a surface area of 100*110 microns, and only 40 in $PbZr_{0.52}Ti_{0.48}O_3$ (PZT) for the same surface area. This result is due to the different mechanical and piezoelectric properties of the two materials.

It may be possible to improve the performance of the devices described in Figure 2 by using different materials. For example, the piezoelectric effect is much stronger in PZT [17] compared to ZnO. This is immediately evident from comparing the peak voltages in Figure 5 for the same applied force. PZT however is more difficult to grow as high quality nanowires. We have also investigated using $Gd_5Si_2Ge_2$ as the phase change material. While making the fabrication more challenging, the $G_5Si_2Ge_2$ response to temperature changes is significantly greater than NiTi, and is expected to result in an increased output voltage. Modeling of these devices in multiphysics codes such as COMSOL using $Gd_5Si_2Ge_2$ should be possible if the materials properties are known. For $G_5Si_2Ge_2$, the results for strain along different directions of a single crystal have recently been published [18].

It should also be possible to improve the design for the current ZnO nanowire devices. From the simulations, the maximum voltage would be achieved for 50 nanowires on a surface area of 100*110 microns. This gives a density of nanowire which is 4,500 nanowires/mm^2. An estimate from Figure 2 gives approximately 3000 nanowires/mm^2, so we might expect a 50% increase in the OCV with additional nanowires in the device fabrication. It is also clear from Figure 2 that the nanowires are not perfectly aligned as in the simulation, so this also provides an opportunity for further improvements.

One particular area of interest is the expected efficiency for harvesting either mechanical or thermal energy using the ZnO nanowire devices described here. It is difficult to quantify efficiencies for the mechanical harvesting since it will depend in large part on the type of overall MEMS device in which the nanowire harvester is placed [19-20]. It is possible to say something about the limits of thermal harvesting efficiency by comparing the Carnot efficiency of the compound thermoelectric with the efficiency of a common thermoelectric material such as Bi_2Te_3. For the 50^{o}C temperature difference from room temperature shown in Figure 4, we would get a Carnot efficiency of slightly less than 10%. For Bi_2Te_3 at a 50^{o}C difference, we expect an efficiency of less than 2% [21-22]. This implies there is plenty of room for improving on the efficiency of current thermoelectric devices by using compound thermoelectrics for harvesting energy from low quality heat sources.

4. Conclusions

The feasibility of combining a piezoelectric nanowire such as ZnO with a phase change material to harvest both mechanical and thermal energy has been demonstrated. Open circuit voltages of nearly 1V were demonstrated from the ZnO nanowire device in a tapping configuration which emulated a realistic scenario for using human motion as the energy source. When the device was combined with NiTi to create a compound thermoelectric material, open circuit voltages of more than 0.5 V were observed. In both cases, optimization of the nanowire device from materials selection and design geometry bode well for significant improvement over these initial results.

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Conflict of interests

The authors have no conflicts of interest to declare.

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