Supporting Information for
Fabrication of Sub-cell Size "Spiky" Nanoparticles and Their Interfaces with Biological Cells

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S1. Synthesis of Spiky Particles Using High Temperature Deposition Technique.

SiO_2 particles were coated with Au nanoparticles (20 nm) which served as catalyst for Si NW growth. Si NWs were grown on the SiO_2 particles via vapor-liquid-solid (VLS) techniques at 486 ^oC (Figure S1a). However, it was difficult to collect the spiky particles from the supporting substrate due to NWs entangling and particle-substrate fusion after the high-temperature chemical vapor deposition (CVD) process. If sonication or scratching were applied to collect the particles from the substrate, most of the NWs were destroyed (Figure S1b).

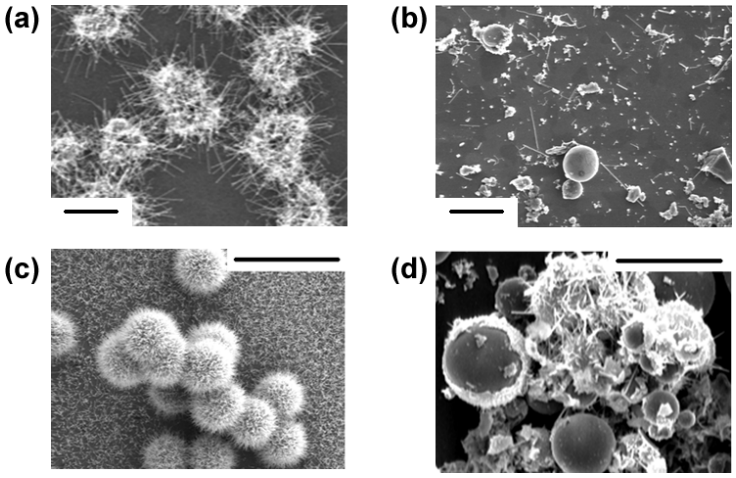

Figure S1. (a) Si NWs grown on SiO_2 particles via VLS method. (b) Most of the Si NWs were destroyed in the particles-substrate separation process. (c) ZnO NWs grown on SiO_2 particles via vapor phase transport deposition. (d) ZnO NWs were destroyed by the attempts to collect particles from substrate. Scale bar: 5 μm.

ZnO NWs can also be grown on particles to produce "spiky particles" using vapor phase transport deposition. A mixture powder of ZnO, SnO, and graphite in a 2:1:1 molar ratio was placed at the center of a quartz tube in a furnace. The mixture was rapidly heated to 900 ^{o}C under a flow of Ar carrier gas at a rate of 70 sccm. SiO_2 nanoparticles were placed on a substrate near the outlet of the quartz tube. ZnO NWs were deposited onto the SiO_2 nanoparticles with 15 min growth time (Figure S1c). However, the ZnO NWs were destroyed after the attempt to collect the spiky particles from the substrate by sonication or scratching (Figure S1d).

S2. The Yield of Spiky Particles (Spiky particle: Nanosphere).

As illustrated in Figure S2a, SiO_2 nanospheres were dropped cast on a glass slide for the ZnO ALD process. The nanoparticles were stacked in multi-layers on the glass substrate. Some nanoparticles present in the deeper layers were not well-coated with ZnO after ALD. Therefore these nanoparticles remained plain after ZnO NWs growth (Figure S2b).

The yield (spiky particle: nanosphere) can be improved by re-drop-casting the ZnO-coated SiO_2 nanoparticles onto a new glass substrate and repeating the ZnO ALD step (Figure S2c). However, this extra ALD step reduced the dispersibility of spiky particles.

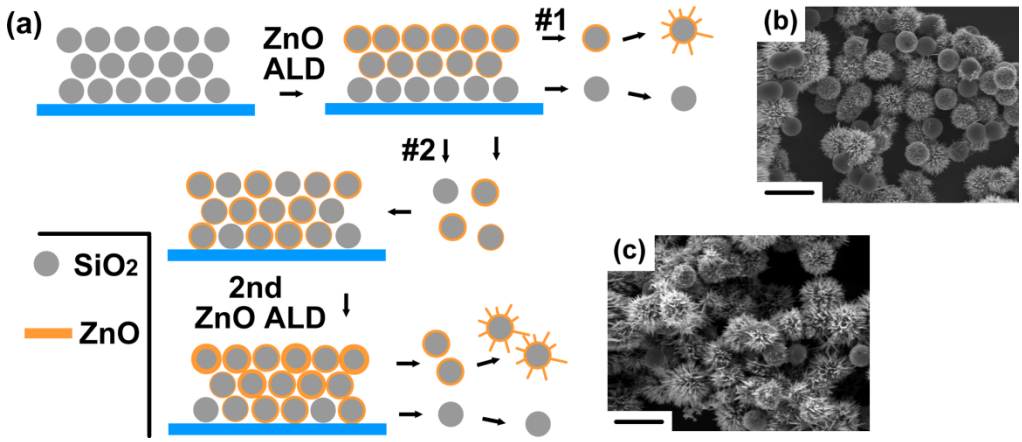

Figure S2. (a) Illustration of ZnO ALD on SiO_2 nanoparticles and repeating ALD step. (b) SEM images of spiky particles. Some particles remain plain after NW growth. (c) The yield of spiky particles was improved by repeating ZnO ALD, yet dispersibility reduced. Scale bar: 2 μm.

S3. Supplemental Data for Cell Interfacing with Spiky Particles.

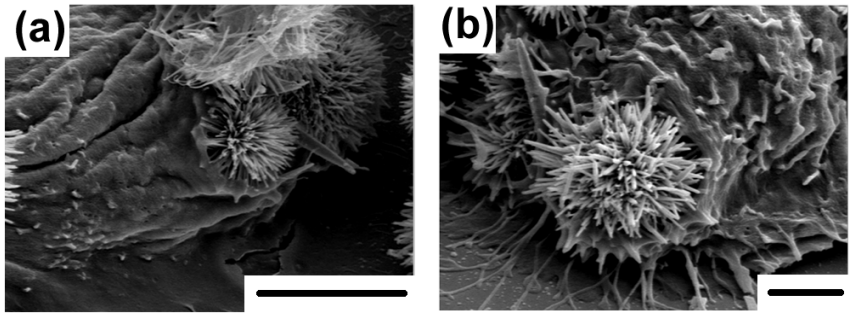

Figure S3. SEM images of spiky particles (based on 2 μm SiO_2 particles) engulfed by CHO cells. Scale bar: 2 μm.

Figure S4 Nanowire dimensions as a function of growth time

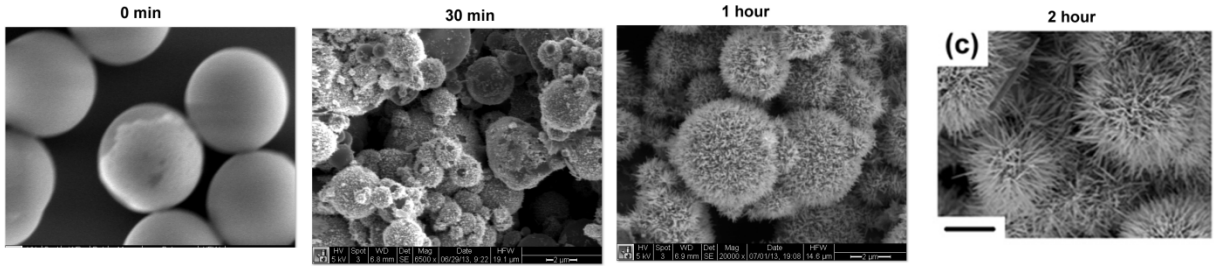

Figure S4. The NW length could be tuned by changing the reaction time from 30 to 120 minutes.

S4. NW Penetration Discussion.

The idea of NW penetration is mostly supported by intracellular drug delivery using NW arrays.[1-5] Intracellular action potentials recorded on neuron cultured on NW array also suggested the direct membrane penetration.[6] Most of the NWs used in these experiments have diameter ~100 nm with aspect ratio (diameter : length) about 10.

On the other hand, NW penetration has not been conclusively visualized with microscopy techniques yet. Cell membrane thickness is only ~5 nm, and the hole size of membrane rupture induced by the NWs may be actually small, so confocal fluorescence microscopy or SEM have limited resolution to determine membrane penetration. TEM technique can provide sufficient resolution,[7] but can only visualize several particular cross sections on a few number of cells. If

the penetration events are rare (only a few NWs penetrating cell membrane[8]), it is difficult to determine penetration with TEM technique.

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