SUPPLEMENTAL INFORMATION

3D Bacterial Flagella as Both Synthetic Biotemplates and Ultrathin Spacers for Enhanced Inter-particle Coupling and Solar Energy Harvesting

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Experimental Methods

Materials.
Polyethylene glycol (PEG, MW 8000), polyethyleneimine (PEI, MW 1800), sodium borohydride ($NaBH_4$), Gold (III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$), polyvinylpyrrolidone (PVP, MW 29000), ascorbic acid and dimethylformamide (DMF) were all purchased from Sigma-Aldrich and used as received.

Amplification and purification of flagella template.
Salmonella serotype Typhimurium were used to produce flagella. The bacteria were cultured in Luria-Bertani (LB) broth medium at 37 °C until OD_{600} reached 0.8, and then were collected through centrifugation. The pellet was re-suspended in phosphate buffered saline (PBS) buffer (pH 7.5) followed by rigorous vortexing, which detached flagella from the surface of bacterial body. After another round of centrifugation, flagella in the supernatant were precipitated by adding the precipitating solution (150 ml per 1 L of supernatant), containing 16.7% (w/v) PEG and 3.3M NaCl. After overnight precipitation at 4 °C, the purified flagella were recovered and redispersed in DI water for future use. The protein concentration was quantified by UV absorption at 280 nm.

Flagella templated assembly of 3 nm AuNPs.
The assembly of AuNPs onto flagella was achieved through electrostatic interaction. The flagella are negatively charged because their constituent protein subunits are anionic. The AuNPs were prepared by $NaBH_4$ reduction of $HAuCl_4$ in the presence of PEI, which endowed the AuNPs positively charged. To assemble AuNPs onto flagella, 1.5 ml of 150 μg/ml flagella in water was added to 5 ml of the prepared AuNPs solution under a proper pH. The mixture was then incubated on a rocker shaker for 30 min, followed by a low-speed centrifugation (2000 g) to remove the unassembled AuNPs. After another attempt of washing by water, the resultant pellet containing AuNPs-flagella complexes was collected and resuspended into 500 μl DI H_2O for further seeded growth.

Seeded growth of 3D Au nanochains.
To a 5 ml solution containing 100 μl of washed AuNPs/flagella assemblies, 400 μl of 5 wt% PVP and different amounts (3, 9, 27 or 81 μl) of 60 mM $HAuCl_4$, 1 ml of 10 mM ascorbic acid was added dropwise under gentle stirring. Afterwards, another 30 min stirring was performed to complete the reaction. The post-grown 3D nanochains were collected and re-dispersed in H_2O for optical property study, or in ethanol for thin film fabrication.

Atomic force microscopy (AFM) characterization.
The image of the 3D nanochains composed of 50 nm AuNPs was collected using a Bruker atomic force microscopy (AFM). The height distribution of the nanochains was analyzed using the free Gwyddion software.

Simulation of optical properties.

The simulations for standard 1D, 2D and 3D nanochains in Figure 1 were carried out using the discrete dipole approximation (DDA) and T-Matrix method. The simulation for the synthesized 3D nanochains on the flagella template were carried out using the DDA method. The DDA method is a numerical method to calculate the optical properties of structures of different shape, size, and composition. In the DDA methods, the particles were presented with an array of polarizable cubes.

Fabrication of thin films with 3D nanochains and 50 nm AuNPs.

The 3D nanochains composed of 50 nm AuNPs were used for solar film fabrication. 3 ml of a concentrated nanochains solution in ethanol were added onto a piece of copper substrate (size: ~5 cm×5 cm×0.13 cm; weight: ~29 g, purchased from onlinemetals.com, used as received), which had been sealed by glass slides along the edges to prevent leakage. The sample was air-dried and the resultant black film had a coated area of 4.5 cm × 3.3 cm.

The 50 nm spherical AuNPs used for fabrication of control films were prepared through a seeded method. Briefly, 13 nm citrate-coated AuNPs were first synthesized following a reported method.[1] The citrate ligands were then replaced by PVP through overnight rigorous stirring. Then, the PVP-coated AuNPs were centrifuged and re-dispersed into ethanol in 5 times of the original concentration. To obtain 50 nm AuNPs, 4.4 ml of 0.1 M ascorbic acid in methanol was added dropwise into the growth solution, which contained 120 μl of 60 mM $HAuCl_4$ in ethanol, 16 ml of 3% (w/v) PVP in DMF, and 80 μl of the seed solution. The reaction was allowed to continue overnight under gentle stirring. Afterwards, the AuNPs were collected by centrifugation and concentrated into ethanol. The AuNPs control film was made using the same amount of gold and by the same evaporation method as the 3D nanochains.

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) characterization.

The morphology of flagella purified from Salmonella Typhimurium were characterized by Zeiss 10A TEM after negative staining using 1 % (w/v) uranyl acetate (UA). The as-assembled and post-grown 3D nanochains were directly observed without staining. The film samples were first sputter coated with iridium and the SEM measurements were carried out using a Zeiss NEON high resolution SEM.

Optical characterization.

The absorption spectra of as-assembled and seeded-grown nanochains in solutions were measured by UV/Vis spectrometer (IMPLEN). For thin films, a FieldSpec 3 spectroradiometer (ASD Inc.) was employed to collect the diffusion reflection spectra of the samples. The absorption spectra were then calculated using the equation: %absorption = 100% - diffusion reflectivity.

Measurement of solar-thermal conversion.

The 3D nanochains and free AuNPs films on copper plates, as well as a pristine copper plate, were placed in the open air. A type k thermocouple probe was taped to the edge of the copper substrates, and the temperature was read using a digital multimeter. Sunlight was simulated using a xenon lamp, and was output through a heat resistant optical fiber. Simulated sunlight with an average power density of 0.11 and 0.5 W/cm^2 (highest output intensity of our simulated sunlight source) was considered equivalent to 1 time and 4.5 times of that of the natural sunlight, respectively. For all light-related tests, the substrates were irradiated by simulated sunlight at an angle of 90°.

Solar-thermal heat based electricity generation.
A commercial TEG unit (TECTEG, TEG1-1268-4.3) was used for the tests. The device was assembled by sandwiching the TEG unit in between the 3D nanochains film coated copper plate and an aluminum heat sink, with the hot side of the unit in contact with copper plate and the cold side with the heat sink. The assembled device was tightened with screws to ensure good thermal contact between different components. When testing the device under simulated sunlight, the heat sink was placed half way underwater at room temperature. The voltage generated and the surface temperature of the copper plates were collected using a digital multimeter. The thermal images were taken using an infrared camera (ICI 7320P). All the tests were conducted under ambient conditions.

Supplementary Figures

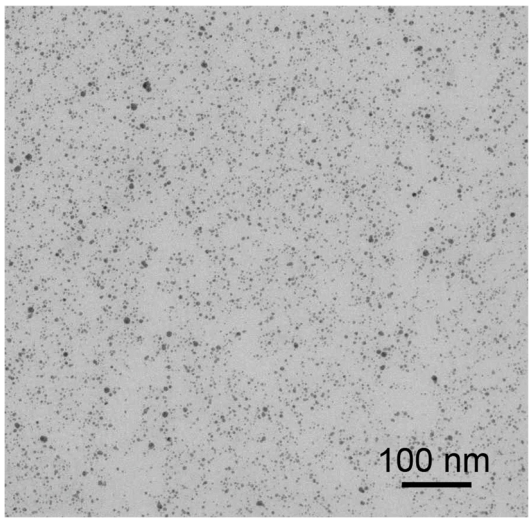

Figure S1. TEM image of PEI coated AuNPs. The average diameter is about 3 nm.

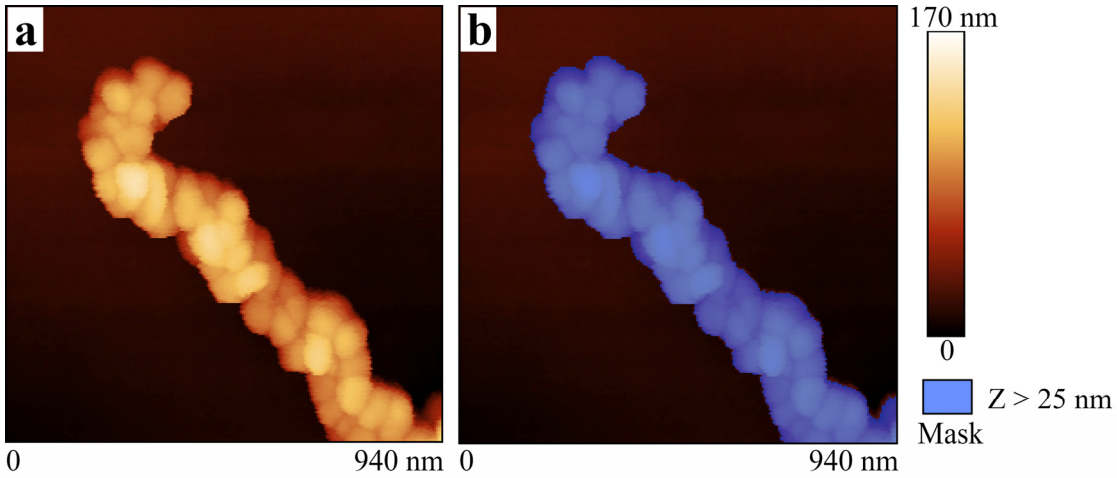

Figure S2. a) 2D AFM image of a single 3D nanochain with the AuNPs size of 50 nm. b) Blue masked area: nanochain image with the data points (corresponding to the height below a certain threshold value) removed from (a). This kind of image was used for height distribution analysis generating Figure 2i.

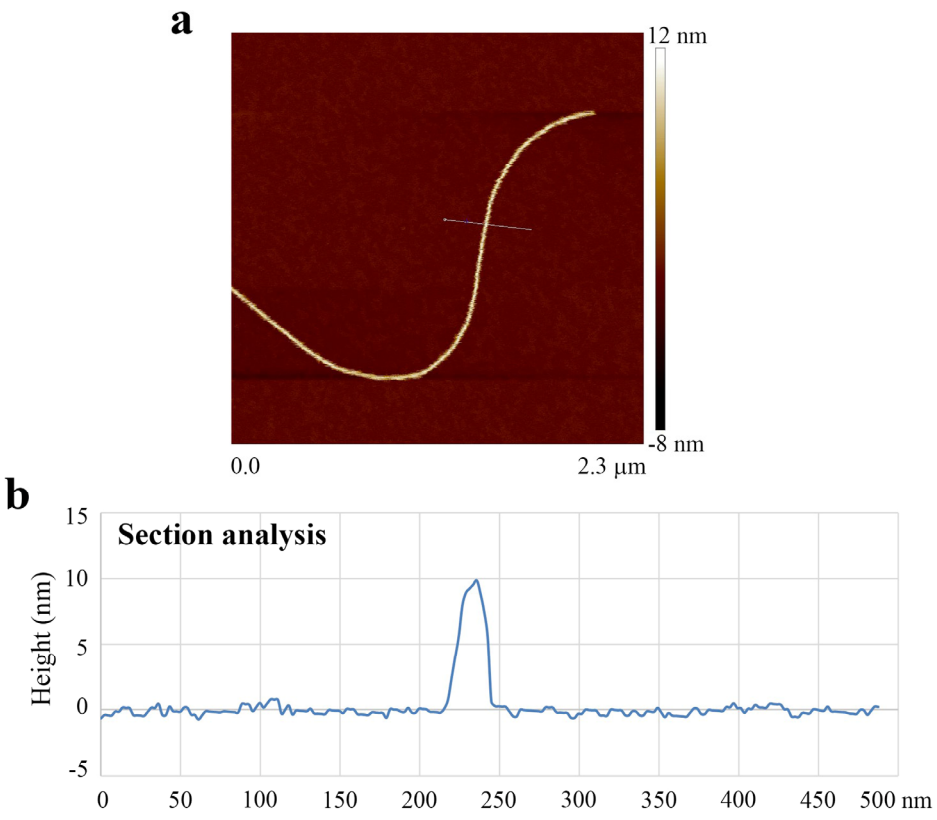

Figure S3. AFM image (a) and the corresponding height profile (b) of a flagellum nanofiber. The width of flagella measured by TEM is about 14 nm, but the height of flagella measured here by AFM is about 10 nm. The difference suggests that flagella may have been flattened to some extent when they are dried from the bulk liquid phase.

Figure S4. Solutions of AuNPs nanochains after seed-mediated growth of flagella-templated AuNPs. The amount of flagella and attaching seeds was fixed in each solution, and the amount of HAuCl4 was increased from left to right. From left to right, the colors are light red, light purple, dark purple and greyish black, respectively. The average AuNPs sizes are 8, 14, 28 and 50 nm corresponding to the structures in Fig. 3c-f, respectively.

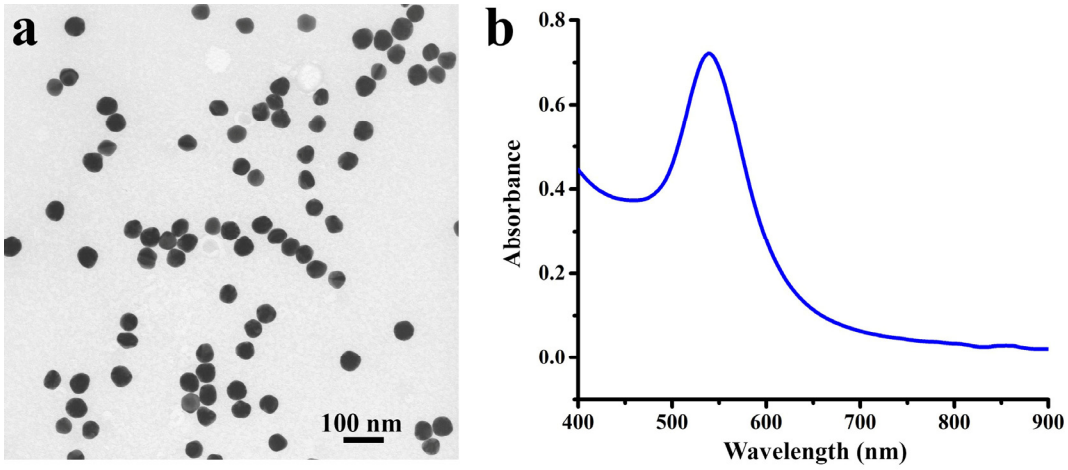

Figure S5. TEM and optical spectrum of the 50 nm AuNPs used for AuNPs-based film fabrication.

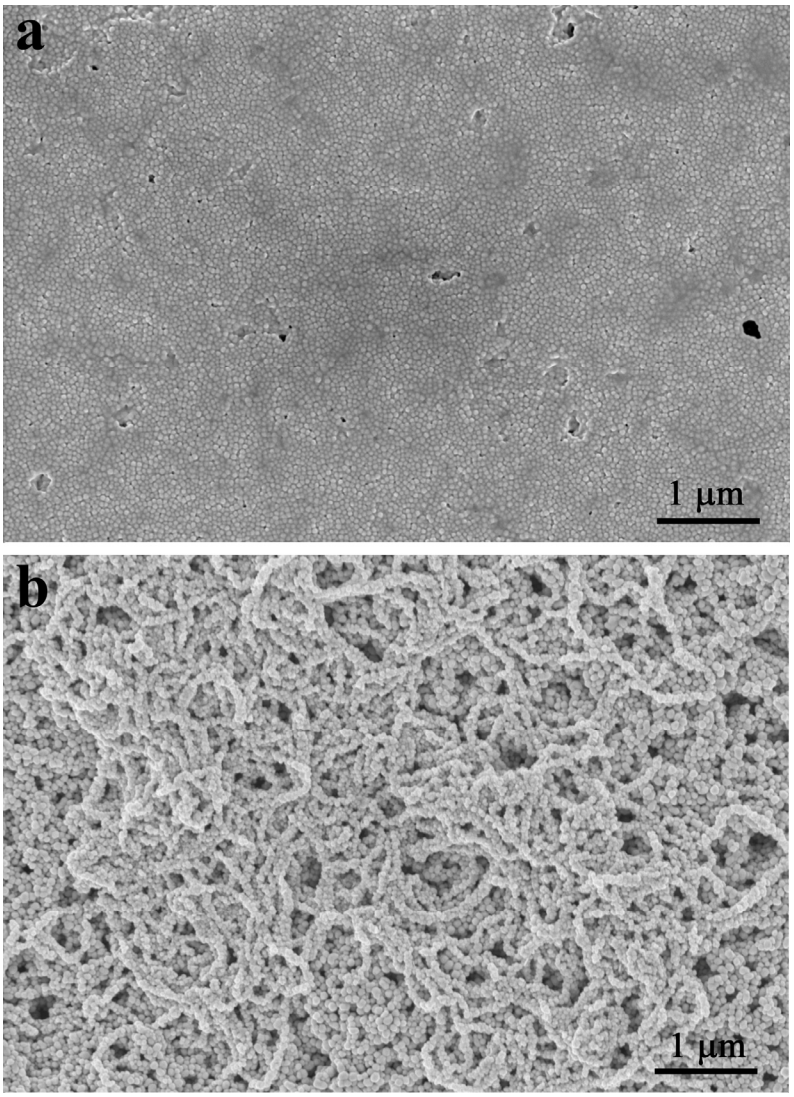

Figure S6. SEM images of AuNPs film and 3D nanochains film at a low magnification. a) AuNPs film. b) nanochains film.

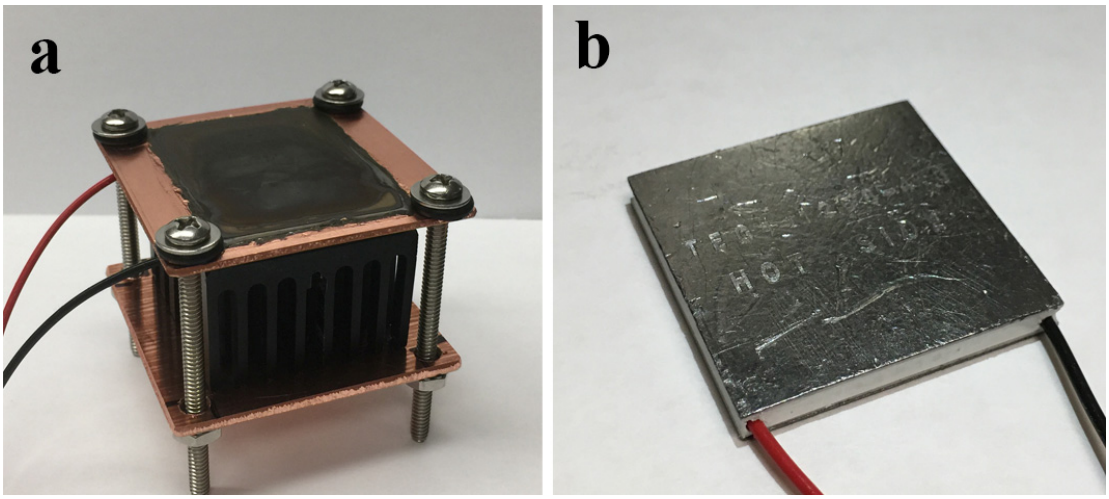

Figure S7. a) Top side view of the energy converting device. In the image, the top copper plate was coated by a 3D Au nanochains film (black colored area). b) Commercial TEG unit. The lateral length is 35 mm and the overall thickness is 3 mm. Both the top and the bottom, known as the hot and the cold sides, are graphite sheets, and the thermal electric modules are sandwiched in between them. The red and black cables are for electricity output. The Au nanochains film coated Cu plate which converted light to heat was placed at the hot side.

Table S1. Solar-thermal conversion efficiency under irradiation power density of 1S and 4.5S.

Materials	Efficiency under 1S	Efficiency under 4.5S
Cu	18.9%	17.8%
AuNPs/Cu	42.4%	42.6%
3D-NCs/Cu	88.1%	84.9%

Reference

1. N. G. Bastus, J. Comenge and V. Puntes, *Langmuir*, 2011, **27**, 11098-11105.