

## Supporting Information for

# Electrospun Micropatterned Nanocomposites Incorporated with Cu<sub>2</sub>S Nanoflowers for Skin Tumor Therapy and Wound Healing

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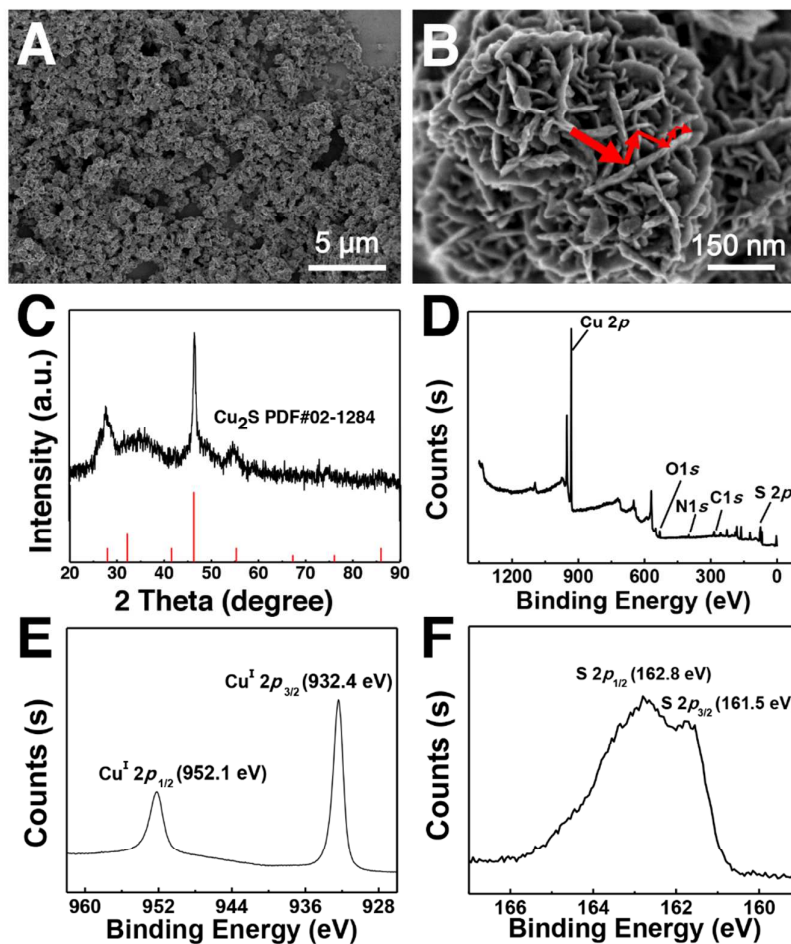
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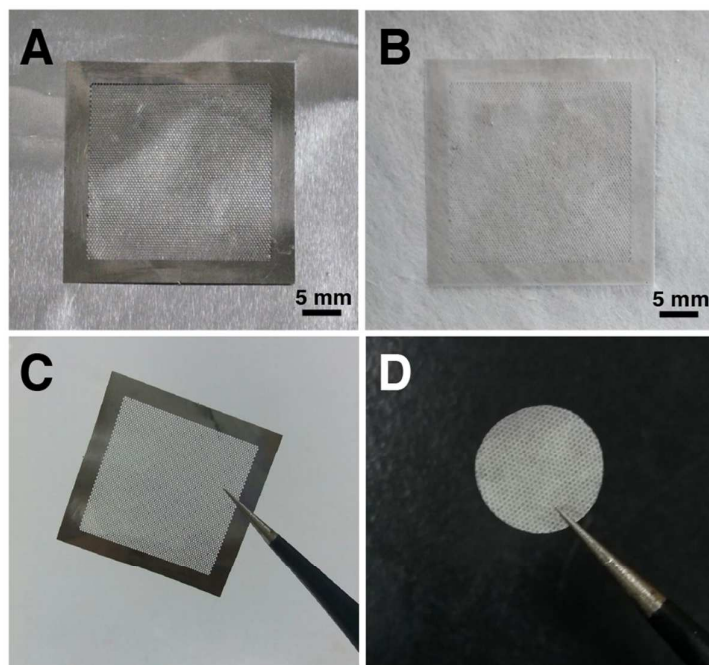
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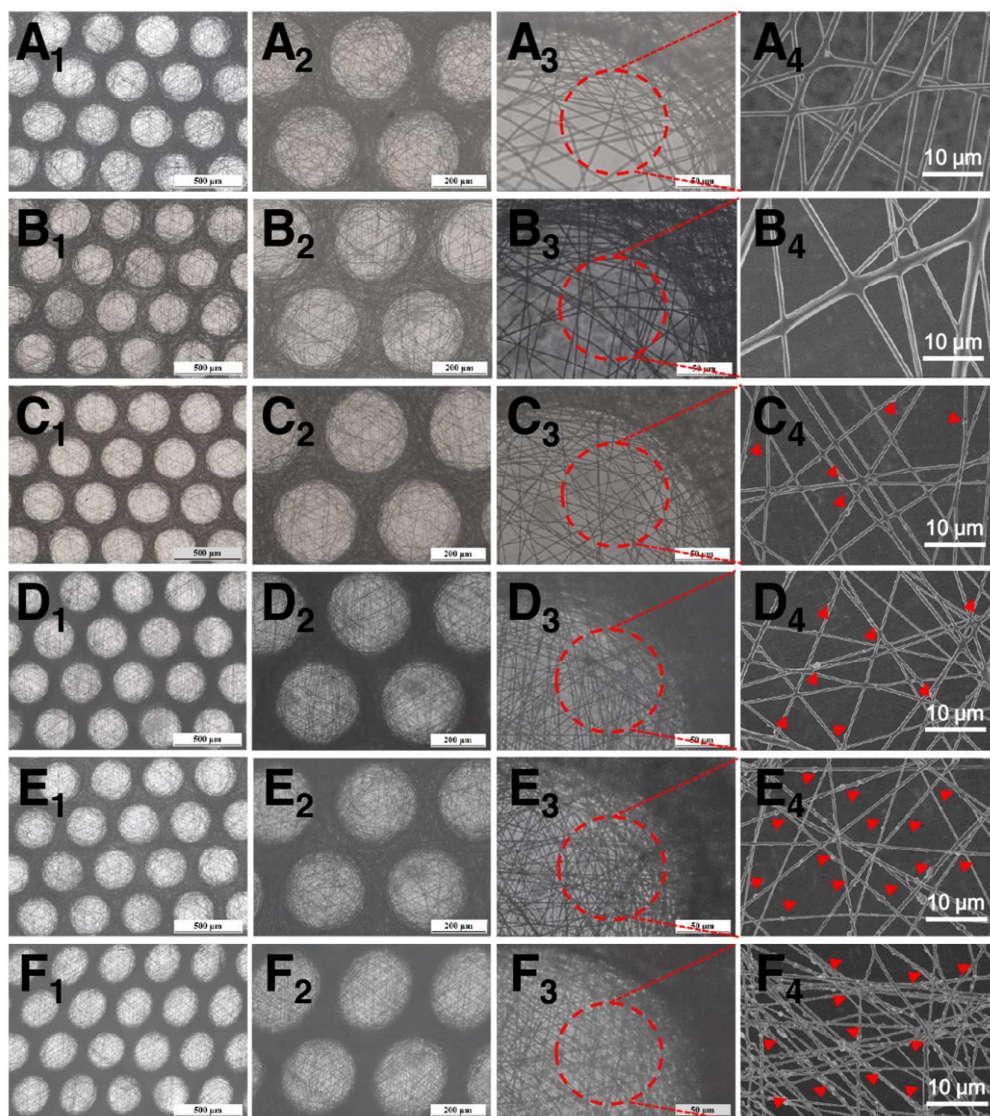
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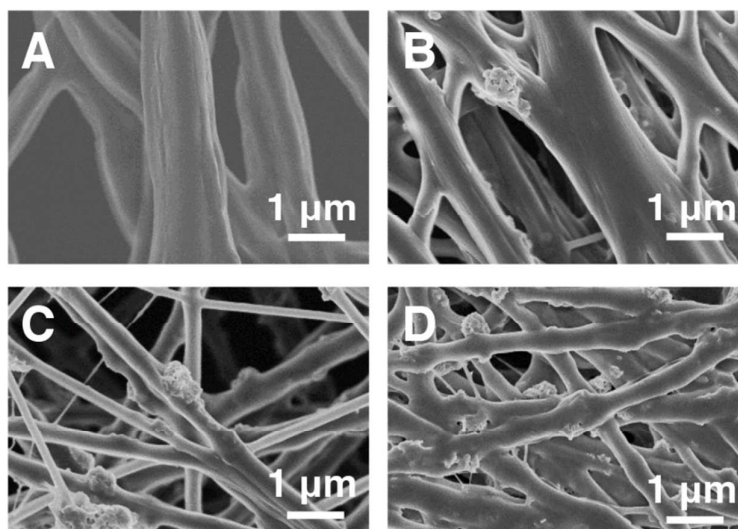
**Figure S1.** Characterization of  $\text{Cu}_2\text{S}$  particles. (A, B) SEM images, (C) XRD pattern and (D) XPS spectrum of  $\text{Cu}_2\text{S}$  particles. XPS characteristic spectrum for (E) Cu 3p and (F) S 2p electrons of  $\text{Cu}_2\text{S}$  particles, indicating valence state of +1 and -2 for Cu and S, respectively.



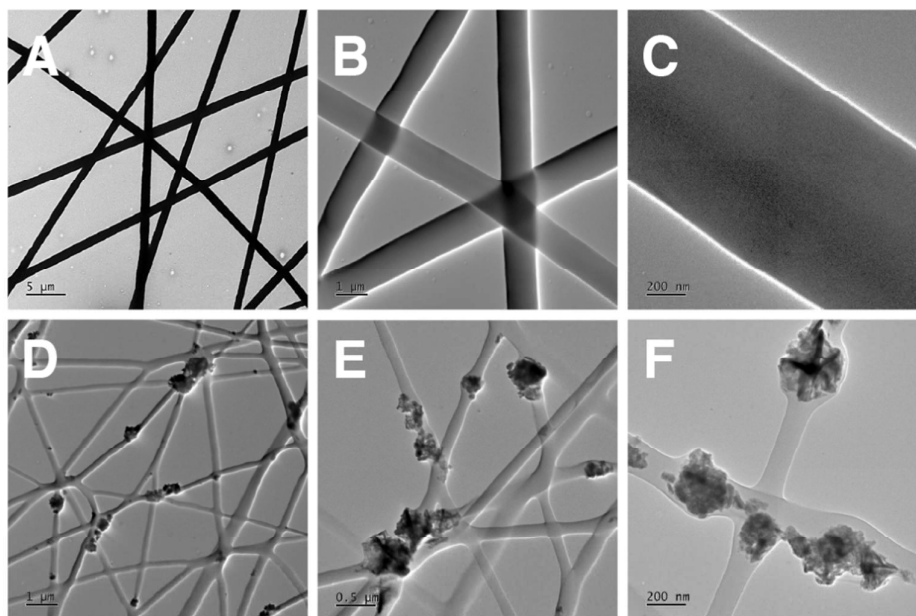
**Figure S2.** Photograph of (A) a custom-made stainless steel mesh (pore diameter: 300  $\mu\text{m}$ ) horizontally fixed on the conductive plate as the fiber collector, (B) electrospun fibers directly deposited on the surface of the mesh, (C) a steel mesh and (D) CS-PLA/PCL membranes (diameter: 10 mm) held by tweezers.



**Figure S3.** Morphologies of CS-PLA/PCL membranes. Representative optical images of (A<sub>1-3</sub>) 0CS-PLA/PCL, (B<sub>1-3</sub>) 10CS-PLA/PCL, (C<sub>1-3</sub>) 20CS-PLA/PCL, (D<sub>1-3</sub>) 30CS-PLA/PCL, (E<sub>1-3</sub>) 40CS-PLA/PCL, (F<sub>1-3</sub>) 50CS-PLA/PCL membranes at different magnification and corresponding (A<sub>4</sub>-F<sub>4</sub>) SEM images of fibers in the micropatterned macropores of CS-PLA/PCL membranes, indicating the successful integration with Cu<sub>2</sub>S nanopaticles (shown by red arrows) into the polymer fibers.

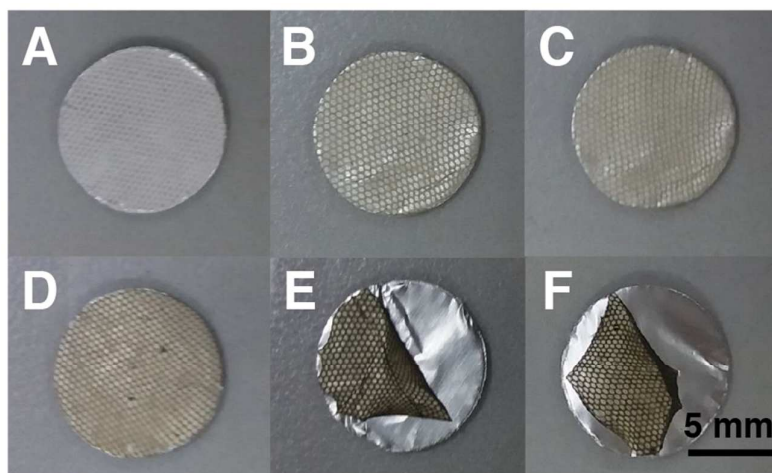


**Figure S4.** Representative high-resolution SEM images of (A) 10CS-, (B) 20CS-, (C) 40CS- and (D) 50CS-PLA/PCL membranes. With the increase of  $\text{Cu}_2\text{S}$  content in the precursor dispersion, the particle amount in the fibers proportionally increased.

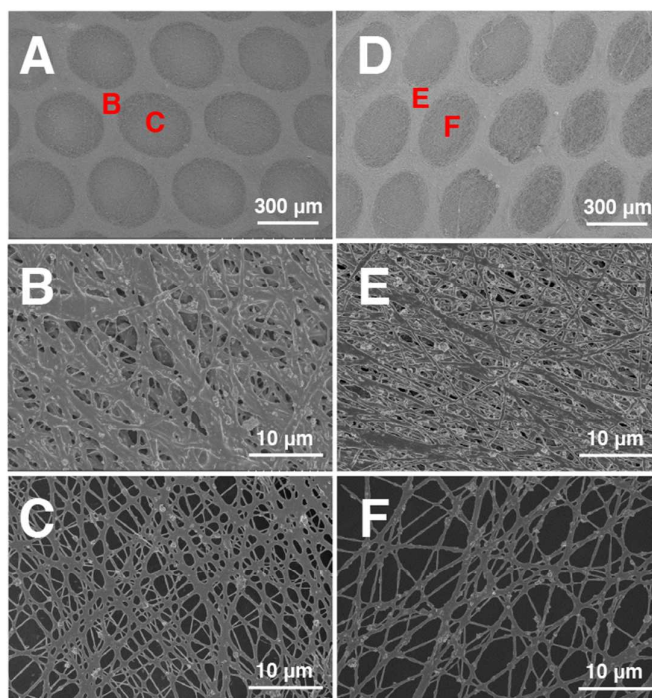


**Figure S5.** Representative TEM images of (A-C) 0CS- and (D-F) 30CS-PLA/PCL membranes at different magnification. The particles could not be fully embedded into the  $\text{Cu}_2\text{S}$ -incorporated electrospun fibers, which led to the fibers with rougher surface than unloaded membranes.



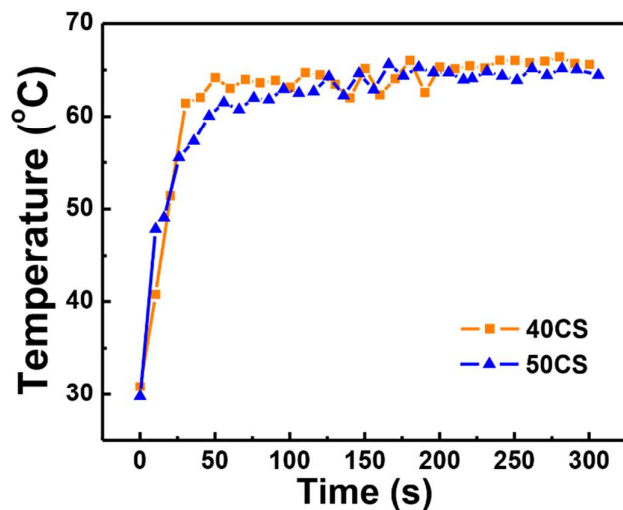


**Figure S6.** Photographs of (A) 0CS-, (B) 10CS-, (C) 20CS-, (D) 30CS-, (E) 40CS- and (F) 50CS-PLA/PCL membranes physically fixed on aluminum foils after exposure to 808-nm laser irradiation under dry condition at the power density of  $0.50 \text{ W}\cdot\text{cm}^{-2}$  for 5 min. 0CS-, 10CS-, 20CS- and 30CS-PLA/PCL membranes showed no obvious change in shape under irradiation as compared to the seriously damaged morphologies of 40CS- and 50CS-PLA/PCL membranes.

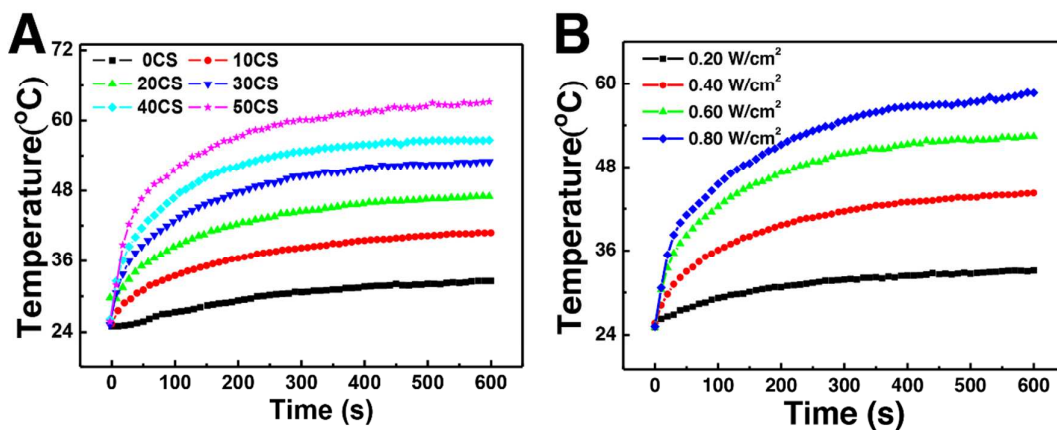


**Figure S7.** Representative SEM images of (A-C) 30CS- and (D-F) 40CS-PLA/PCL membranes under dry condition after exposure to 808-nm laser irradiation at the power density of  $0.50 \text{ W}\cdot\text{cm}^{-2}$  for 5 min. (B, E) and (C, F) shows the dense and loose fibrous structure in different membrane regions indicated in (A, D) at high magnification, respectively. 30CS-PLA/PCL membranes preserved better macroporous patterned structures than 40CS-PLA/PCL membranes after irradiation.



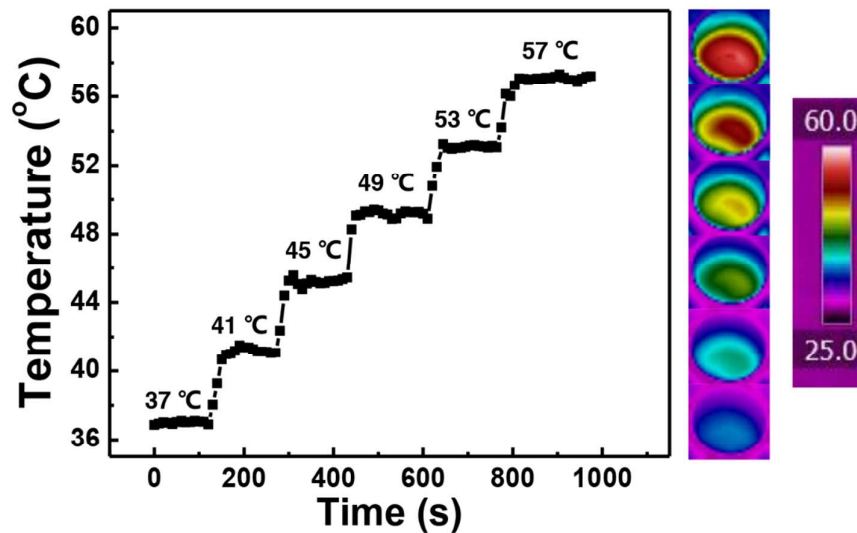


**Figure S8.** Photothermal heating curves of 40CS- and 50CS-PLA/PCL membranes in the dry environments under continuous irradiation of the 808-nm laser at  $0.50 \text{ W}\cdot\text{cm}^{-2}$  for 5 min.

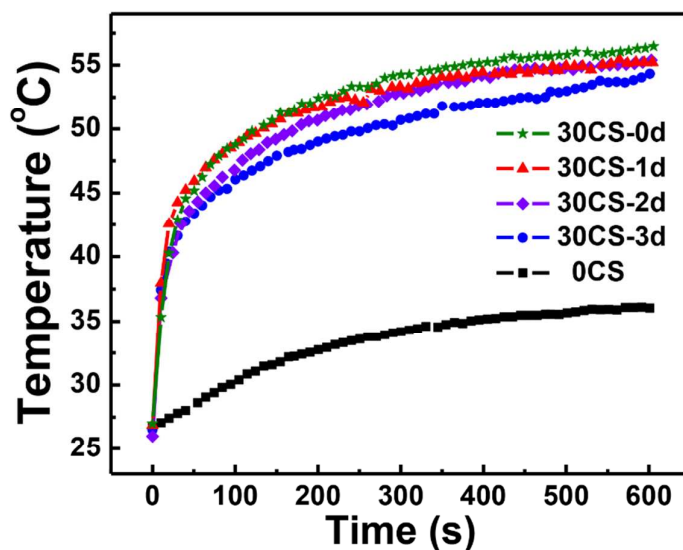


**Figure S9.** Photothermal heating curves of CS-PLA/PCL membranes immersed in 500 mL phosphatic buffer solution (PBS) under 808-nm laser irradiation with (A) different  $\text{Cu}_2\text{S}$  contents at power density of  $0.50 \text{ W}\cdot\text{cm}^{-2}$  and (B) 30CS-PLA/PCL with various power densities indicated for 10 min. The photothermal temperature could be efficiently controlled between room temperature and  $62^\circ\text{C}$  by altering laser power densities and  $\text{Cu}_2\text{S}$  contents.

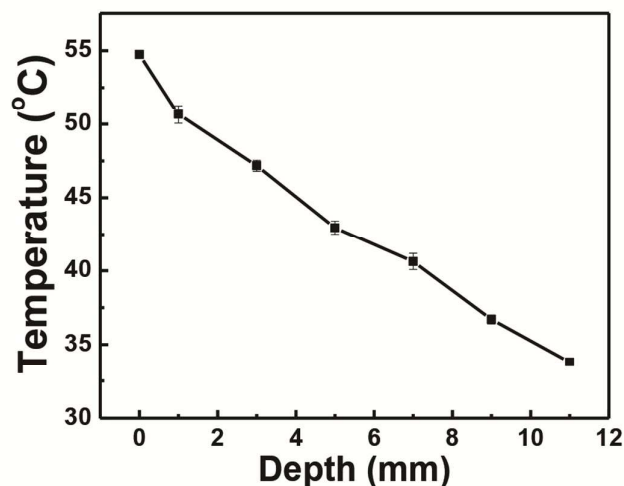




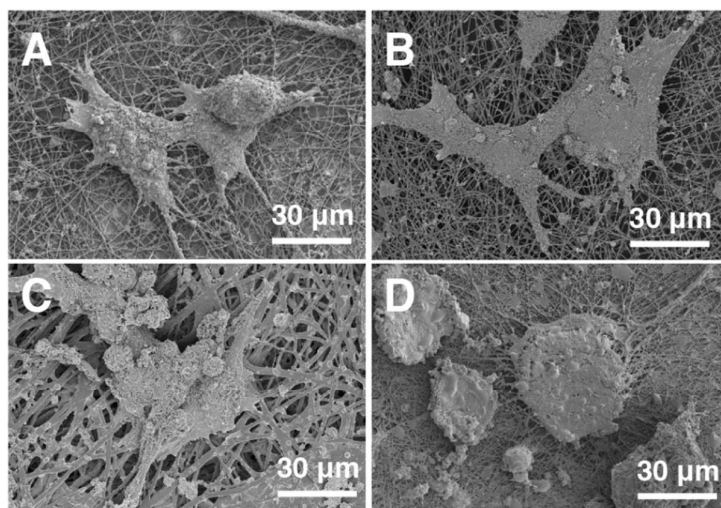
**Figure S10.** Heating curves and the corresponding near infrared images of 30CS-PLA/PCL membranes with controllable temperature under the wet condition.



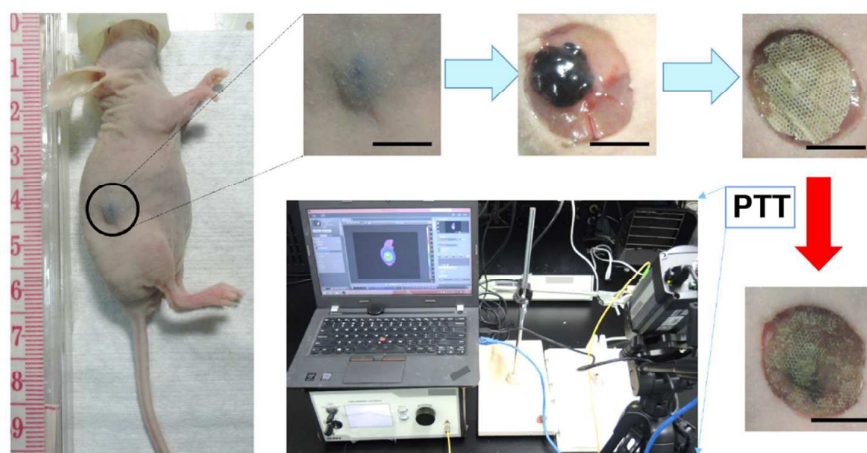
**Figure S11.** Photothermal heating curves of 30CS-PLA/PCL membranes after being soaked in cell medium for 0, 1, 2, 3 days ( $0.60 \text{ W} \cdot \text{cm}^{-2}$ , 10 min,  $37^\circ \text{C}$ ).  $\text{Cu}_2\text{S}$ -incorporated membranes could remain their excellent photothermal performance with slightly decrease in temperature elevation.



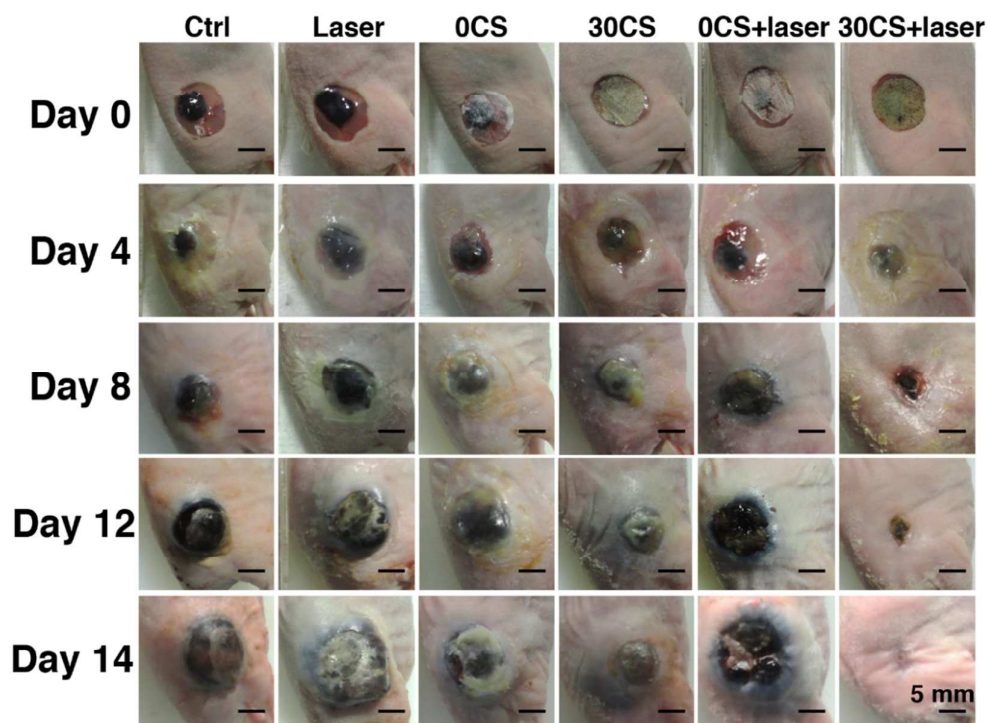
**Figure S12.** Final temperature of the pork at various depths (0, 1, 3, 5, 7, 9 and 11 mm), top of which was covered by 30CS-PLA/PCL membranes and then irradiated by the 808-nm laser at the power density of  $0.40 \text{ W} \cdot \text{cm}^{-2}$  for 10 min at room temperature.



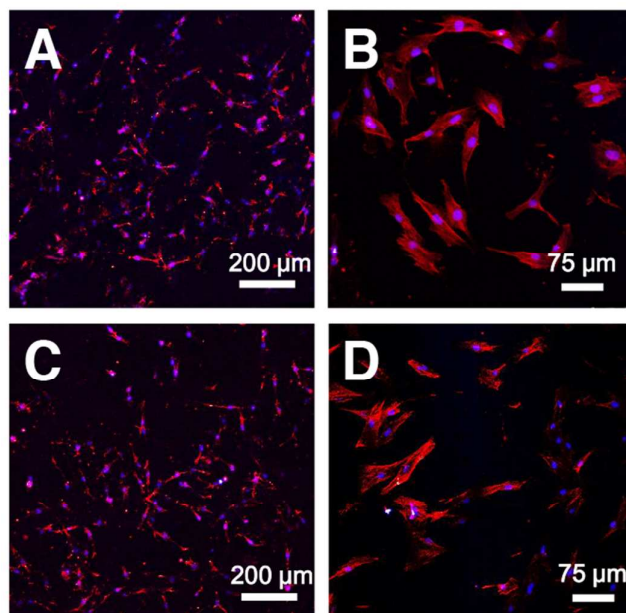
**Figure S13.** Morphologies of skin tumor cells after photothermal therapy. SEM images of skin tumor cells (murine B16F10 melanoma cells) on membranes treated with (A) 0CS- or (B) 30CS-PLA/PCL membranes without laser irradiation and (C) 0CS- or (D) 30CS-PLA/PCL membranes with laser irradiation (808 nm,  $0.50 \text{ W} \cdot \text{cm}^{-2}$ , 15 min). The cellular morphologies in the three control groups kept unchanged with affluent pseudopods, while the tumor-cell morphology was seriously damaged in the laser-irradiated 30CS-PLA/PCL membranes.



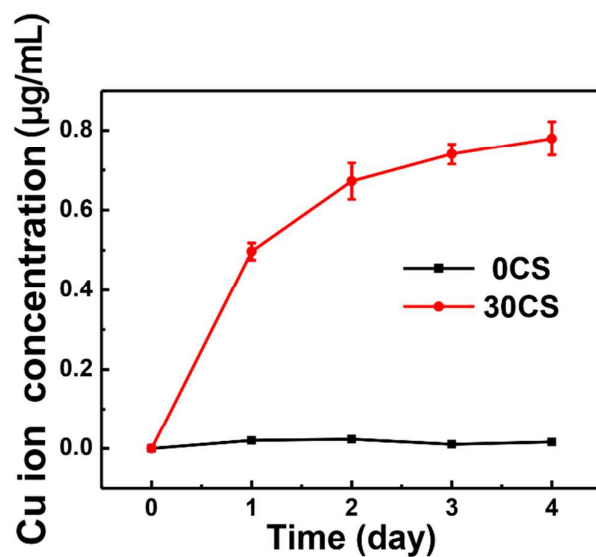
**Figure S14.** Experimental procedure of *in vivo* photothermal therapy. A full thickness wound (diameter = 10 mm) was created in the tumor site of tumor-bearing mice. 30CS-PLA/PCL membranes were used to cover the wound area, which was then exposed to the 808-nm laser irradiation at a power density of  $0.40 \text{ W} \cdot \text{cm}^{-2}$  for 15 min. Scale bar, 5 mm.



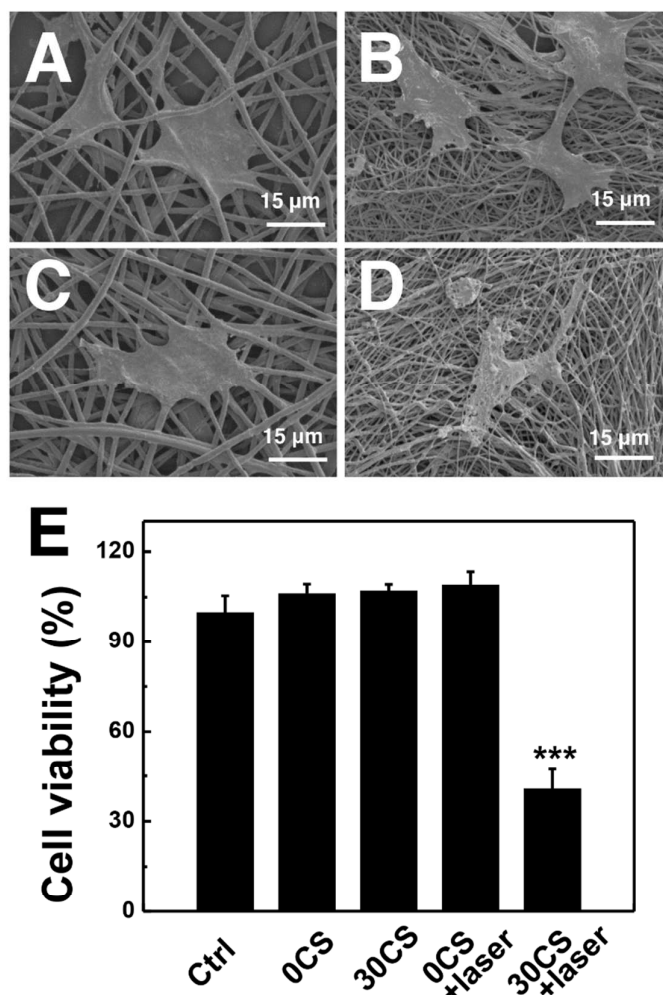
**Figure S15.** Representative skin wound photographs of tumor-bearing mice treated after various different treatments indicated taken on day 0, 4, 8, 12 and 14. Scale bar: 5 mm. The tumor volume of the 30CS-PLA/PCL+laser group was reduced after 4 days of irradiation, gradually disappeared with black scars left at the original sites after 8 days and the wound even completely healed without tumor recurrence within 14 days.



**Figure S16.** Morphologies of skin cells attached to CS-PLA/PCL membranes. Confocal LSM (red: cytoskeleton; blue: cell nuclei) images of human dermal fibroblasts (HDFs) after seeding on the (A, B) 0CS-PLA/PCL or (C, D) 30CS-PLA/PCL membranes for 24 h. Both 0CS- and 30CS-PLA/PCL membranes supported the adhesion and spreading of skin cells.



**Figure S17.** Cumulative amount of Cu ions released from 0CS- and 30CS-PLA/PCL membranes into Dulbecco's modified Eagle's medium (DMEM) as a function of immersion time at 37 °C.



**Figure S18.** The photothermal effect on normal skin cells. Representative SEM images of human umbilical vein endothelial cells (HUVECs) on membranes treated with (A) 0CS- or (B) 30CS-PLA/PCL membranes without laser irradiation and (C) 0CS- or (D) 30CS-PLA/PCL membranes with laser irradiation (808 nm,  $0.50 \text{ W} \cdot \text{cm}^{-2}$ , 15 min). (E) Relative cell viability of HUVECs treated with 0CS- or 30CS-PLA/PCL membranes without NIR treatment and 0CS- or 30CS-PLA/PCL membranes with NIR treatment (808 nm,  $0.50 \text{ W} \cdot \text{cm}^{-2}$ , 15 min). The cellular morphologies were seriously damaged in the laser-irradiated 30CS-PLA/PCL membranes as compared to other three control groups, indicating normal skin cells could be killed by 30CS-PLA/PCL membranes under NIR irradiation.