Supporting Information

Experimental Section

1. Preparation of the aligned CNT sheet and fiber.

The aligned CNT sheet was dry-drawn from the spinnable CNT array synthesized by chemical vapor deposition in a tube furnace.[1-2] The chemical-vapor-deposition (CVD) conditions were carefully optimized to ensure that the CNT sheet could be continuously drawn from the CNT array. The catalysts of Al_2O_3 (3 nm) and Fe (1.2 nm) were successively deposited on a silicon wafer by electron beam evaporation with deposition rates of 2 and 0.5 Å s^{-1}, respectively. During the CVD process, Ar (400 sccm) was firstly used for 8 min to fully remove the air in the tube furnace. Afterwards, the ethylene (90 sccm) which served as the carbon precursor and a mixture of Ar (400 sccm) and H_2 (30 sccm) which served as the carrier gases, were supplied. The growing time was 10 min at 740 ℃ to prepare the spinnable CNT array. The aligned CNT sheet was dry-drawn from the spinnable CNT array using a knife. The aligned CNT fiber was prepared by further twisting of the aligned CNT sheet. The diameter, layer and length of the CNT among the resultant array/sheet was in small ranges of 8-12 nm, 5-8 layers and 200-300 μm, respectively.

2. Preparation of the photo-to-electricity system.

The aligned CNT sheet with thickness of ~90 nm, length of 2.5 cm and width of 1.0 mm was dry-drawn from the spinnable CNT array onto a poly(ethylene terephthalate) separator with thickness of 0.05mm, length of 2.5 cm and width of 1.0 mm. The separator was used to avoid the short circuit between the two electrodes and also the light irradiation to the back electrode. The aligned CNT sheet with the same area and thickness was drawn on the other side of the separator. Ethanol was dropped onto the CNT sheets and separator to avoid the CNTs being peeled off the separator. The similar method was used to prepare photo-to-electricity system using CNT fiber with length of 2.5 cm. The CNT/ZnO composite electrode was prepared by dropping 30 μL dispersion of ZnO particles (nano-zinc oxide, 99.9%, metal basis, Aladdin, 81.37(Mw)) (1 g ZnO/10 mL water) onto the CNT sheet with area of 1 mm×2.5 cm and thickness of ~90 nm. The CNT sheet needed to be pre-treated by oxygen plasma to improve its hydrophilicity. The same two CNT/ZnO composite electrodes were assembled into the electricity generation system.

3. Measurements for electricity generation.

Copper wires and silver paste were used to connect the two electrodes composed of the aligned CNT sheets for measurement. The photo-to-electricity system was put on water with one electrode upward and another electrode downward. It should be noted that the silver paste and copper wires were made to have no contact with water to avoid the influence of the interaction of metals and water on the voltage output of the system. Simulated light shone from the above and irradiated only onto the upper CNT. The open-circuit voltage and short-circuit current between the two electrodes were recorded at an electrochemical workstation (Metrohm, Autolab PGSTAT204).

4. Characterization

The structures were characterized by scanning electron microscopy (Ultra 55, Carl Zeiss). The photographs were taken by a camera (Nikon, J1). The simulated sunlight was generated by a solar simulator with AM1.5 solar light (LanshengXQ350W, Shanghai, equipped with a 350 W Xe lamp and an AM1.5 filter-typical solar spectrum). The ultraviolet light illumination was obtained by using a CEL-LT90 and UVREF to obtain light with wavelengths below 400 nm. The visible light illumination was obtained by using a UVIRCUT420 to obtain light with wavelengths between 420 and 780 nm. The infrared light illumination was obtained by using a VISCUT800 to produce the light with wavelengths above 400 nm. The light intensity was calibrated using a reference Si solar cell (Oriel-91150). Electron paramagnetic resonance signals of radicals trapped by 5,5-dimethyl-1-pyrroline-N-oxide (DMPO, Dojindo Laboratories (Kumamoto, Japan)) (30μL/1mL water) were recorded on a JEOL-FA200 spectrometer.

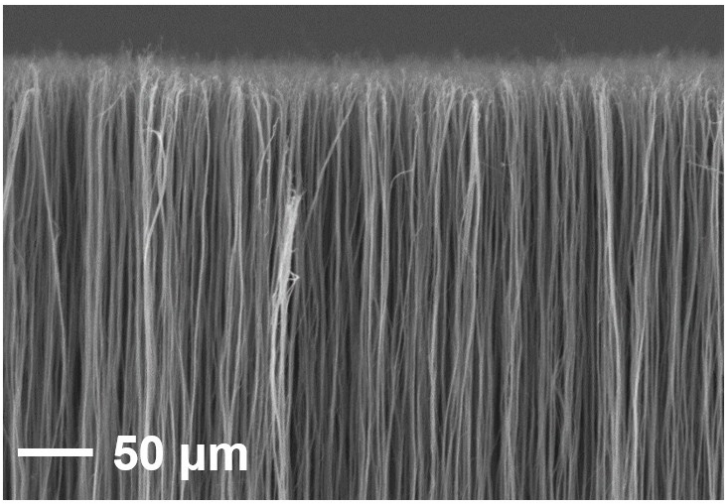

Fig. S1. Scanning electron microscopy image of the CNT array synthesized by chemical vapor deposition method.

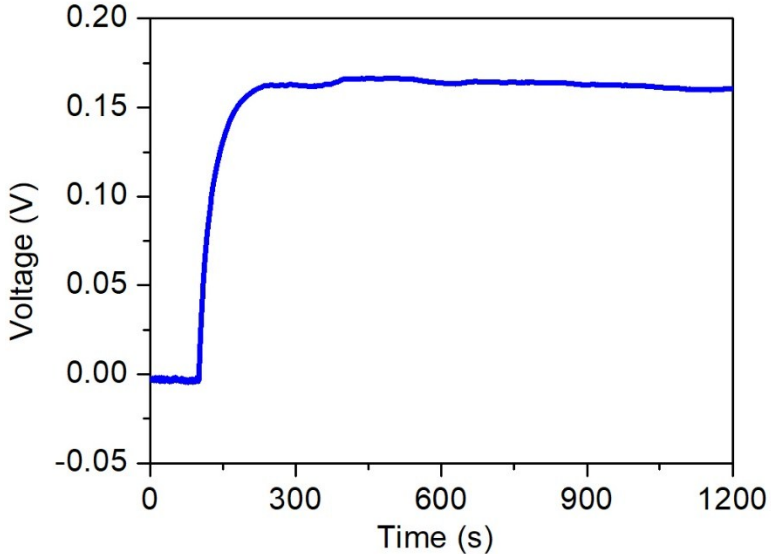

Fig. S2. Open-circuit voltage of the photo-to-electricity system under light irradiation in deionized water with a long duration of 1,000 s.

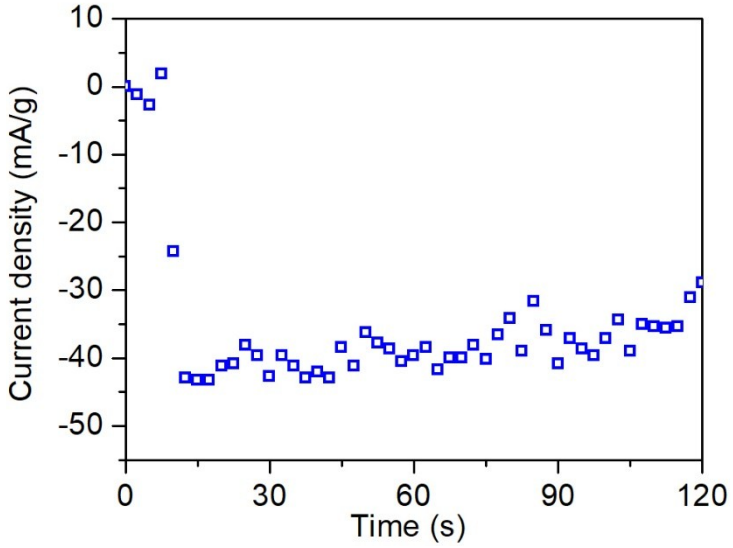

Fig. S3. Short-circuit current density of the photo-to-electricity system under light irradiation in deionized water.

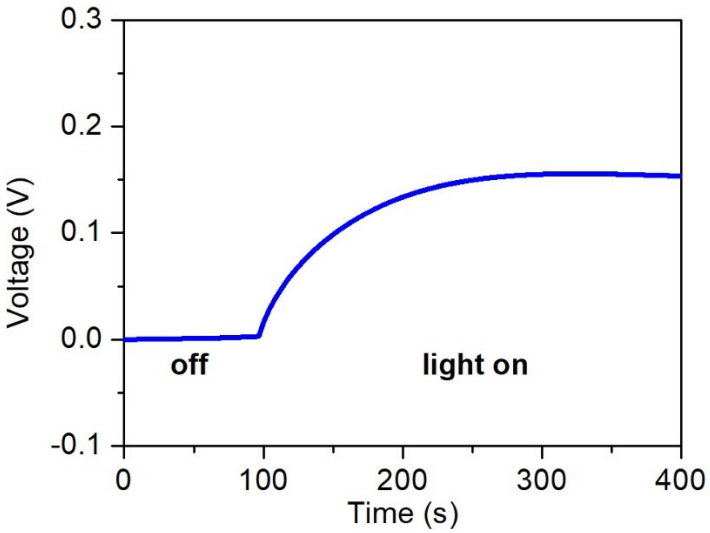

Fig. S4. Open-circuit voltage of the photo-to-electricity system based on CNT fibers upon light irradiation in deionized water.

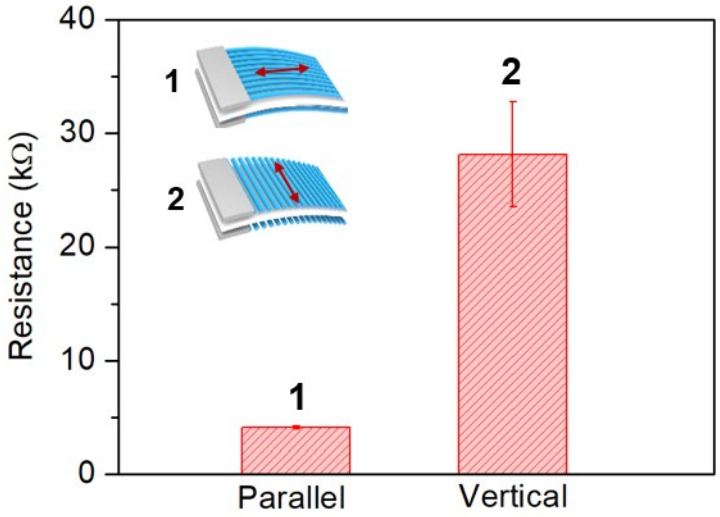

Fig. S5. The resistances of CNT sheets with different aligned directions for the CNTs.

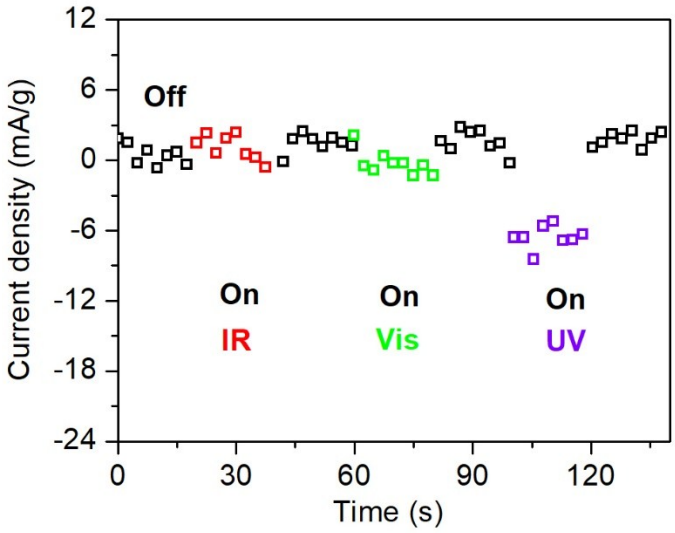

Fig. S6. Dependence of the generated current density on the wavelength of the light.

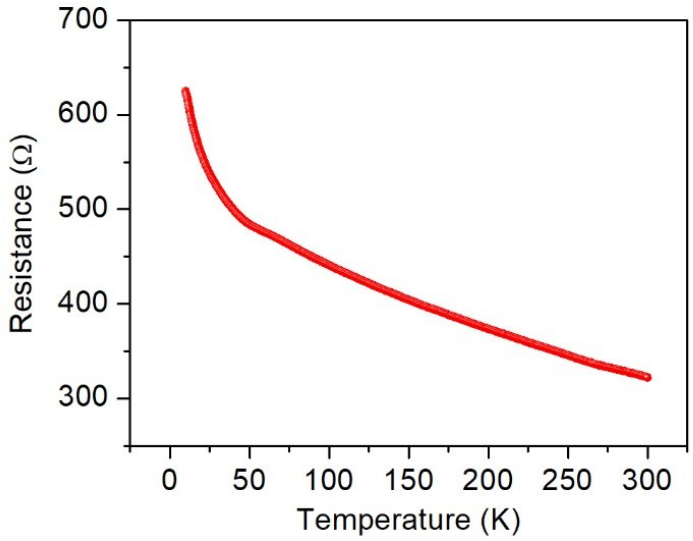

Fig. S7. Dependence of the resistance of CNT sheet on the temperature to verify the semiconducting property of CNT sheet. The size of the CNT sheet was 0.5 cm×0.5 cm.

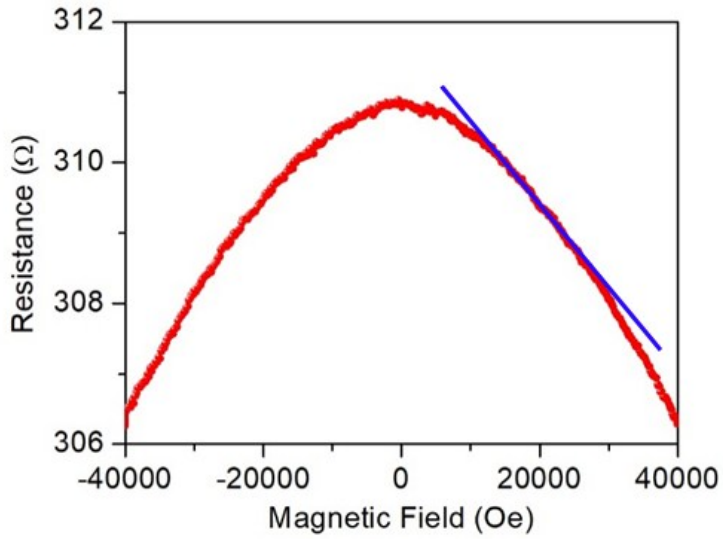

Fig. S8. Dependence of the resistance of CNT sheet on the magnetic field intensity. The hall coefficient is a negative value, indicating that the CNT sheet is an n-type semiconductor and the carriers in CNT sheet are mainly electrons. The size of the CNT sheet was 0.5 cm×0.5 cm.

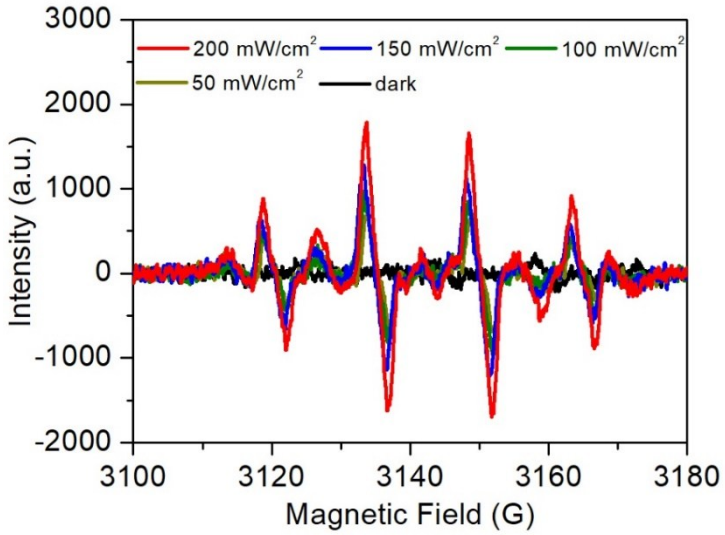

Fig. S9. EPR signals of the DMPO-OH· (aqueous solution) when the device was exposed to the light with different intensity.

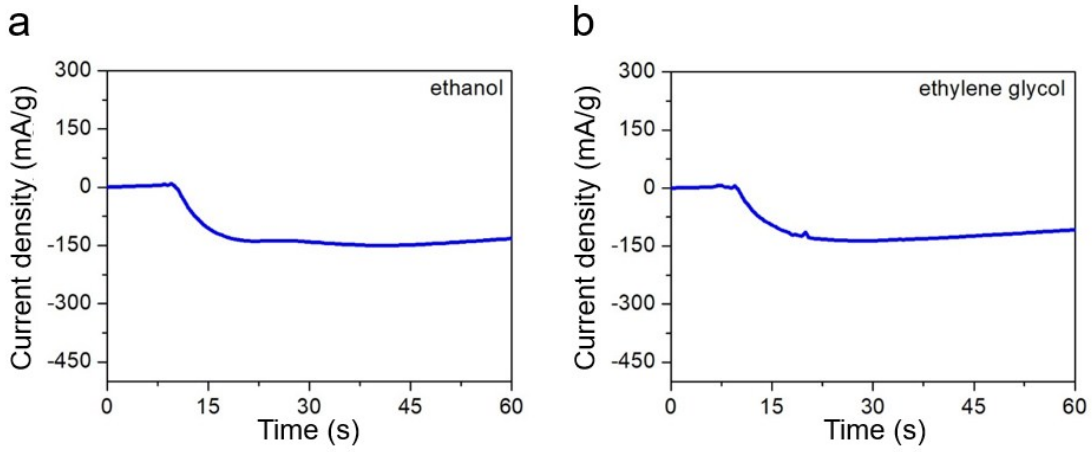

Fig. S10. Current generation of the photo-to-electricity system in ethanol (a) and ethylene glycol (b).

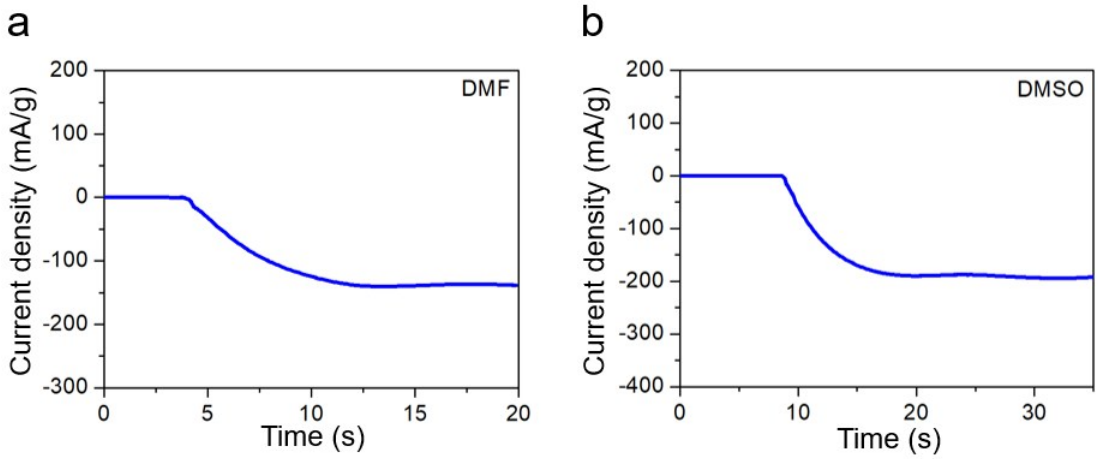

Fig. S11. Current generation of the photo-to-electricity system in DMF (a) and DMSO (b).

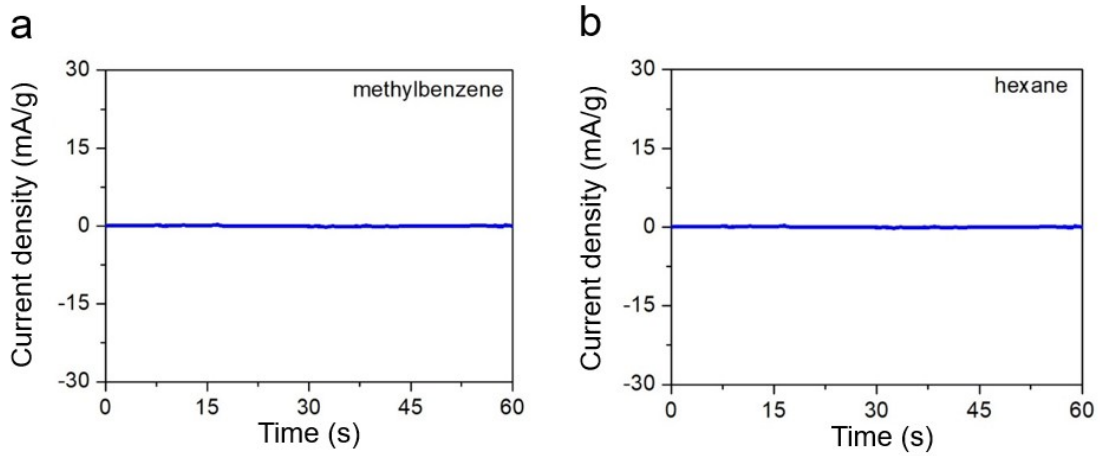

Fig. S12. Current generation of the photo-to-electricity system in nonpolar solvent such as methylbenzene (a) and hexane (b).

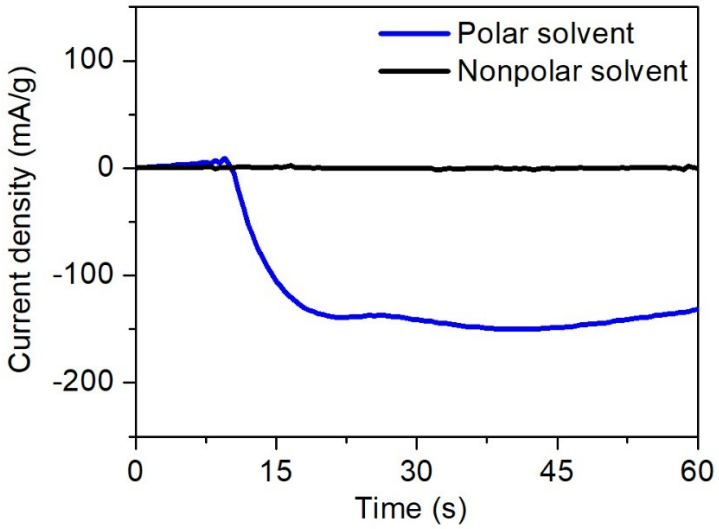

Fig. S13. Current generation of the photo-to-electricity system in polar and nonpolar solvent.

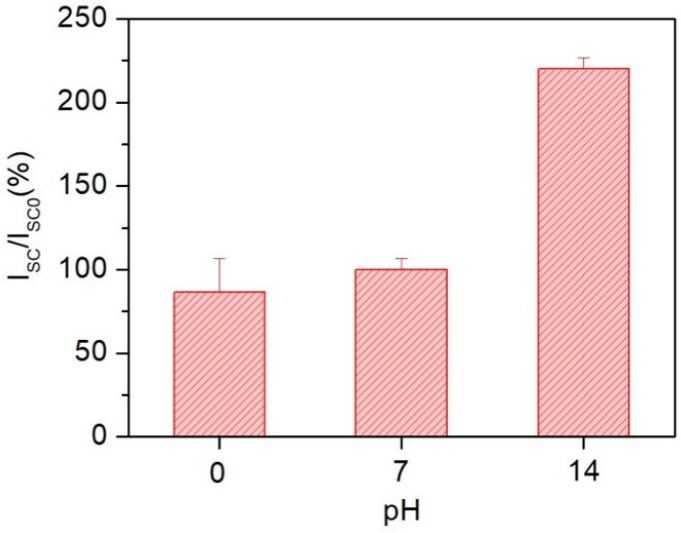

Fig. S14. Short-circuit currents produced by the photo-to-electricity system under a light irradiation in liquids with increasing pH values.

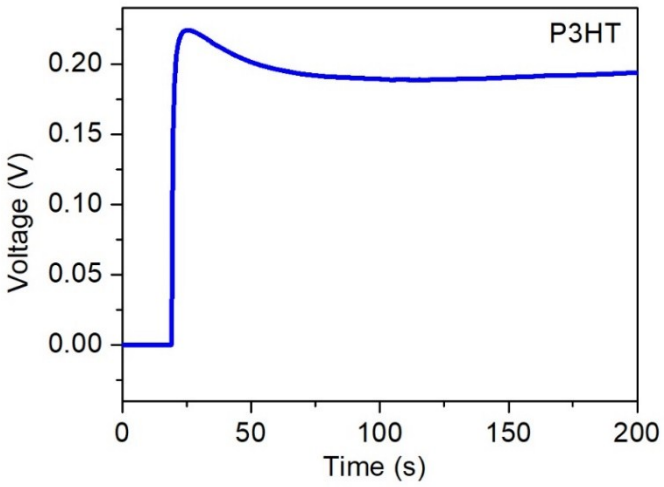

Fig. S15. Electricity produced by the system based on poly (3-hexyl thiophene) (P3HT) under light irradiation in water.

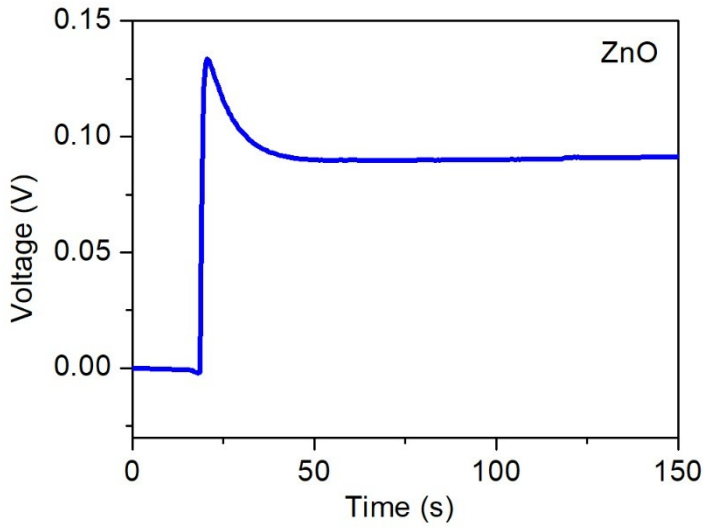

Fig. S16. Electricity produced by the systems based on ZnO under light irradiation in water.

Fig. S17. Photograph of the light-emitting diode powered by ten photo-to-electricity systems connected in series.

References

[1] J. Cao, Y. Zhao, Y. Xu, Y. Zhang, B. Zhang and H. Peng, *J. Mater. Chem. A*, 2018, **6**, 3355-3360.

[2] Y. Zhao, Y. Zhang, H. Sun, X. Dong, J. Cao, L. Wang, Y. Xu, J. Ren, Y. Hwang, I. H. Son, X. Huang, Y. Wang and H. Peng, *Angew. Chem. Int. Ed.*, 2016, **55**, 14384-14388.