Electronic Supplementary Material (ESI) for Energy & Environmental Science.

The bionic sunflower: a bio-inspired autonomous light tracking photocatalytic system

1. Experimental

1.1 Materials

N-isopropylacrylamide (NIPAAm) was purchased from Adamas-beta and recrystallized from hexane. *N,N'*-methylenebis(acrylamide) (bis-AAm), dimethyl sulfoxide and hexane were purchased from Macklin. 2-hydroxy-2-methyl-1-phenyl-1-propanone (Darocur 1173), hydrochloric acid, concentrated sulfuric acid, phosphoric acid, potassium permanganate, hydrogen peroxide, cadmium acetate and thiourea were purchased from Ourchem. Hydrazine monohydrate and acetic acid were purchased from Fisher Scientific. All the chemicals, except NIPAAm, were used as received.

1.2 Preparation of rGO-PNIPAAm hydrogels (RPH)

1.2.1 Preparation of graphene oxide

Graphene oxide (GO) was synthesized by Hummer's method.[1-2] In a typical procedure, 2.0 g of graphite was added into a solution with 240 mL of H_2SO_4 and 27 mL of phosphoric acid, under vigorous stirring. After stirring for 30 min, 12 g of $KMnO_4$ was added into the mixture and the temperature was raised to 50 ℃, which was kept stirring for 12 h. Subsequently, 400 mL of deionized water was added slowly into the solution in an ice bath. 20 mL of 30% H_2O_2 was added dropwise into the above mixture and the mixture was stood overnight. Finally, the solution was washed with 5% aqueous HCl solution and water to remove the residual salts.

1.2.2 Preparation of RPH

The precursor solution for rGO/poly(N-isopropylacrylamide) (PNIPAAm) hydrogel (RPH) was prepared with 40 wt% NIPAAm monomer, 2 wt% crosslinker bis-AAm, 0.35 wt% rGO and 0.5 wt% Darocur 1173 in Dimethyl sulfoxide (DMSO). The prepolymer solution was injected into a capillary (Diameter: 1 mm). The ultraviolet (UV) polymerization underwent for 40 seconds. Then, the rGO/PNIPAAm pillar gel was taken out from the capillary.

1.3 Preparation of CdS/rGO-PNIPAAm hydrogels (CPH)

1.3.1 Preparation of CdS/rGO composite

CdS/rGO composite was prepared *via* a hydrothermal process.[3] Briefly, 0.1589 g of cadmium acetate and 0.1848 g of thiourea were added into a 100 mL beaker with 60 mL of deionized water to form a homogenous solution. Then, 20 mg of GO was added into the solution to form a homogeneous suspension by ultrasonic dispersion. Finally, the mixture was moved into a 100 mL Teflon-lined stainless steel autoclave and reacted under 180 ℃ for 12 h. The product was washed and collected by centrifugation. Finally, the sample was obtained by freeze-drying method.

1.3.2 Preparation of CPH

The precursor solution for CPH was synthesized by mixing 40 wt% NIPAAm monomer, 2 wt% crosslinker bis-AAm, 3 wt% CdS/rGO and 0.5 wt% Darocur 1173 in DMSO. The solution was poured into a flower-shaped mould with a diameter of about 8 mm and cured under UV light for 70 seconds.

1.4 Preparation of bionic sunflower

After the above-mentioned polymerizations of RPH (40 s) and CPH (70 s), the RPH end was fixed with the CPH sheet by adding two drops of RPH precursor solution among their interface. After irradiating the interface with UV light for polymerization (30 s), the two hydrogels can be directly linked with each other forming a complete unit. After that, the RPH component of the bionic sunflower was immersed in 0.3 M of hydrazine aqueous solution for 10 h to reduce GO into reduced GO (rGO). Finally, the bionic sunflower was immersed in deionized water to remove the excess impurities.

1.5 Characterizations

Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy (EDS) were characterized with a HITACHI S-4800 at 30 kV. were taken with a S-4800 (HITACHI). Transmission electron microscopy (TEM) test was carried out on a JEM-2100 (JEOL) electron microscope at an accelerating voltage of 200 kV. X-ray diffraction (XRD) patterns of the samples were measured on a D8 Advance instrument (AXS-Bruker) with Cu Kα radiation. Raman spectra of the samples were recorded at room temperature using Raman microscopes (Renishaw) under an excitation laser wavelength of 532 nm. Ultraviolet visible diffuse reflectance spectra (UV-vis DRS) were recorded on a UV-3600 plus spectrophotometer (Shimadzu) from 400 to 800 nm ($BaSO_4$ as reference material). Fourier transform infrared (FT-IR) spectra were obtained on FALA2000104 (Boman) with KBr as the reference. Mechanical properties of the bionic sunflower were characterized using UTM2203 electronic universal testing machine (load cell = 50 N, Shenzhen Sun Technology Stock Co. Ltd.). Infrared images were characterized with Fluke Thermal Imager.

1.6 Photocatalytic H_2O_2 production test

As a typical run, the photocatalytic synthesis of H_2O_2 was carried out in photocatalytic reactor purchased by PerfectLight. Firstly, six bionic sunflowers were fixed to the bottom of the reactor. Then 100 mL deionized water was added to the reactor and bubbled with O_2 in the dark for 30 min to obtain an O_2 equilibrated environment. The diameter of each stem was 7 mm and its mass was recorded. Afterwards, a 300 W xenon lamp was utilized as the irradiation source. The different incident angles were achieved by changing the angle of the xenon lamp.

H_2O_2 amount was measure by using iodometry.[3-4] Typically, 2 mL of 0.1 M potassium iodide solution (KI) and 0.15 mL of 0.003 M ammonium molybdate solution were added to 20 mL reaction solution, and kept for 10 min. Absorbance at $\lambda = 532$ nm was measured using a UV-Vis spectrophotometer (TU-1901), and then the amount of H_2O_2 generated in the reaction was obtained.

2. Theory and simulation

2.1 COMSOL Multiphysics simulation

In order to simulate the temperature change towards the light under unilateral illumination, finite element analysis was used to simulate it in COMSOL 5.6. Unilateral heating method was used to simulate the temperature rise of hydrogel under irradiation. The finite element method is used to calculate the heat conduction problem, and the heat transfer characteristic of the material is used to solve the problem.

2.1.1 Establishment of model

In COMSOL 5.6, the model is built directly according to the geometry of the sample.

2.1.2 Solid heat transfer

In the model, add the light source to the right column of the model in the form of a heat source. The heat transfer process can be described by the heat transfer equation (1)

$$\rho C_p \frac{\partial T}{\partial t} + C_p u \cdot \Delta T + \nabla \cdot q = Q + Q_{ted} \quad (1)$$

Where $q = -k\nabla T$, ρ is the density of the hydrogel (kg/m^3), C_p is the heat capacity of hydrogel under constant pressure (J/K·kg), k is the thermal conductivity of hydrogel.

The initial temperature is 293.15 K. In order to focus on the temperature change of RPH when irradiation, we set the upper and lower boundary as well as the back side of the RPH as thermal insulation. The insulation surface is set as

$$-n \cdot q = 0 \quad (2)$$

The temperature rises of the bionic sunflower under oblique irradiation, heat flux boundary condition was added to the front side of the model. Select the general inward heat flux. Equation is:

$$q_0 = 4500 \cdot exp(-(z - 0.01)^2 \cdot 50000) \quad (3)$$

Similarly, a convective heat flux is added to the back side of the RPH. As shown in equation (4).

$$q_{0=} = h \cdot (T_{ext} - T) \quad (4)$$

Where h is the heat transfer coefficient (W/m^2 · K), T_{ext} represents external temperature, i.e. water temperature (K).

The parameters are shown in the **Table S1.**

2.2 Density functional theory calculations

The first-principle calculations are performed in the framework of spin-polarized density functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP),[5] with ion-electron interactions depicted by projector augmented waves (PAW) and the exchange and correlation potential described by the function of Perdew, Burke and Ernzerhof (PBE) based on the generalized gradient approximation (GGA).[6-9] Cut-off energy of 400 eV was adopted. In addition, a 2x2x1 Gamma kpoints grids is used to sample the Brillouin zone for the supercell structures. The vacuum space is set to be at least 15 Å to separate the interactions between the neighboring slabs. All the structures are fully relaxed until the force on each atom is less than 0.02 eV $Å^{-1}$. The free energy diagram is defined as the equation (5).

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S \quad (5)$$

where the ΔE is the electronic energy difference, ΔZPE is the change of zero-point energy, T is the temperature (T = 298.15 K), and ΔS is the change of entropy.

3. Supporting figures

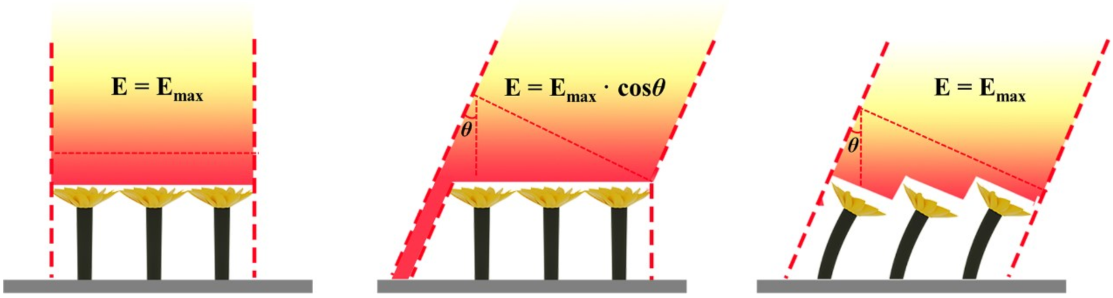

Fig. S1. The phenomenon oblique-incidence energy-density loss and the principle of phototropic behavior to recover energy loss.

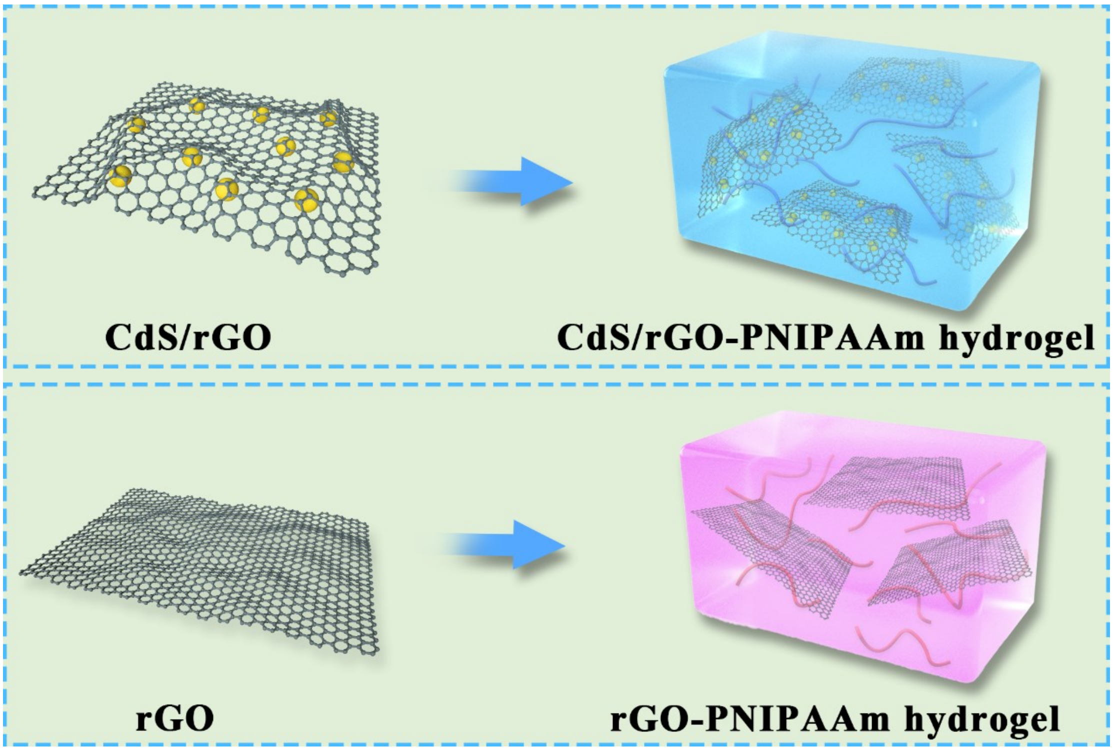

Fig. S2. The preparation processes of (a) CdS/rGO-PNIPAAm hydrogel (CPH) and (b) rGO-PNIPAAm hydrogel (RPH).

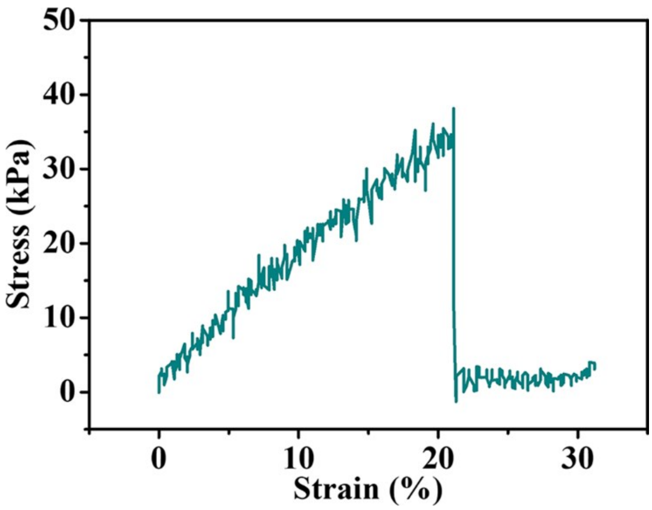

Fig. S3. The stress-strain curve of the bionic sunflower.

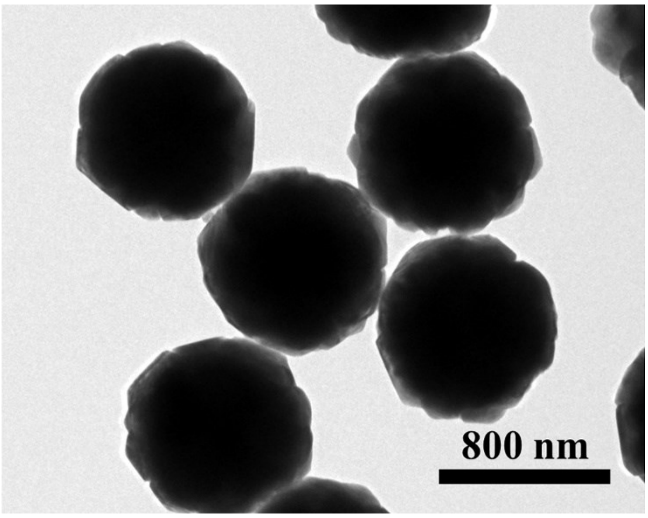

Fig. S4. The TEM image of CdS bulk.

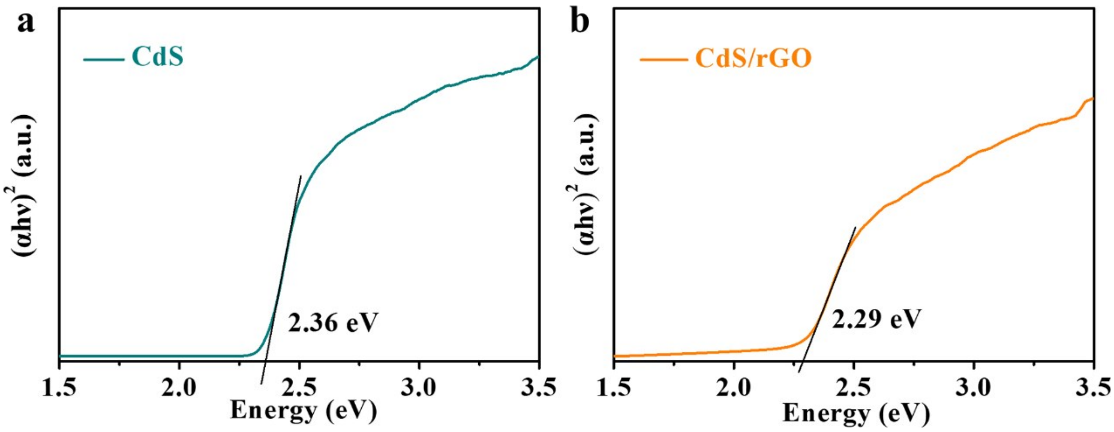

Fig. S5. Plots of $(ah\nu)^2$ *vs.* energy to determine the band gap values of (a) CdS/rGO composite and (b) CdS bulk.

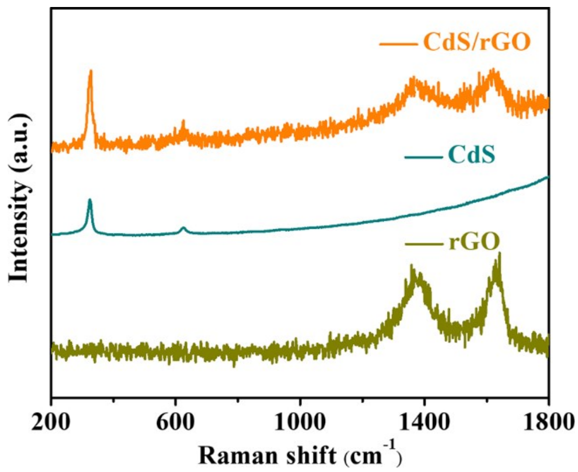

Fig. S6. Raman spectra of rGO, CdS bulk and CdS/rGO composite.

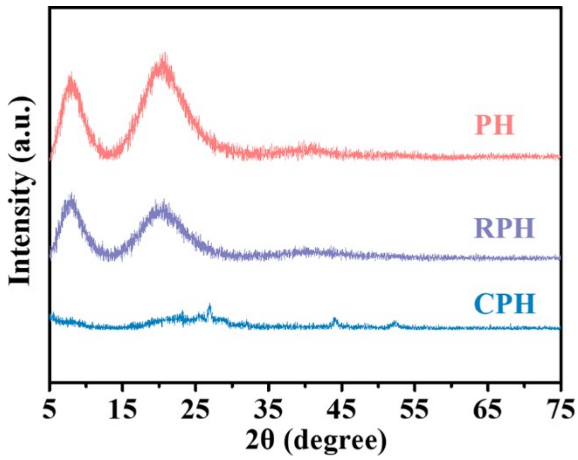

Fig. S7. XRD patterns of PH, RPH and CPH.

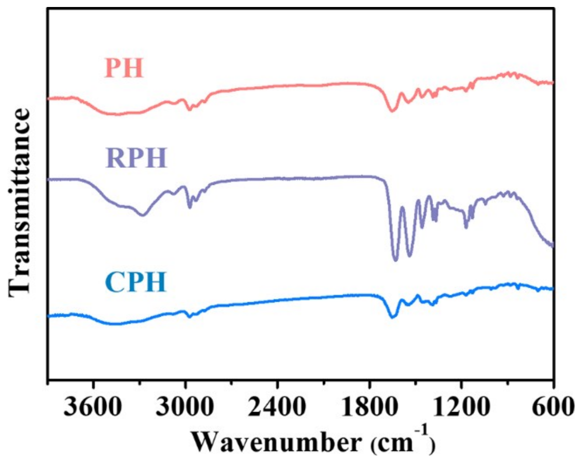

Fig. S8. FTIR spectra of PH, RPH and CPH.

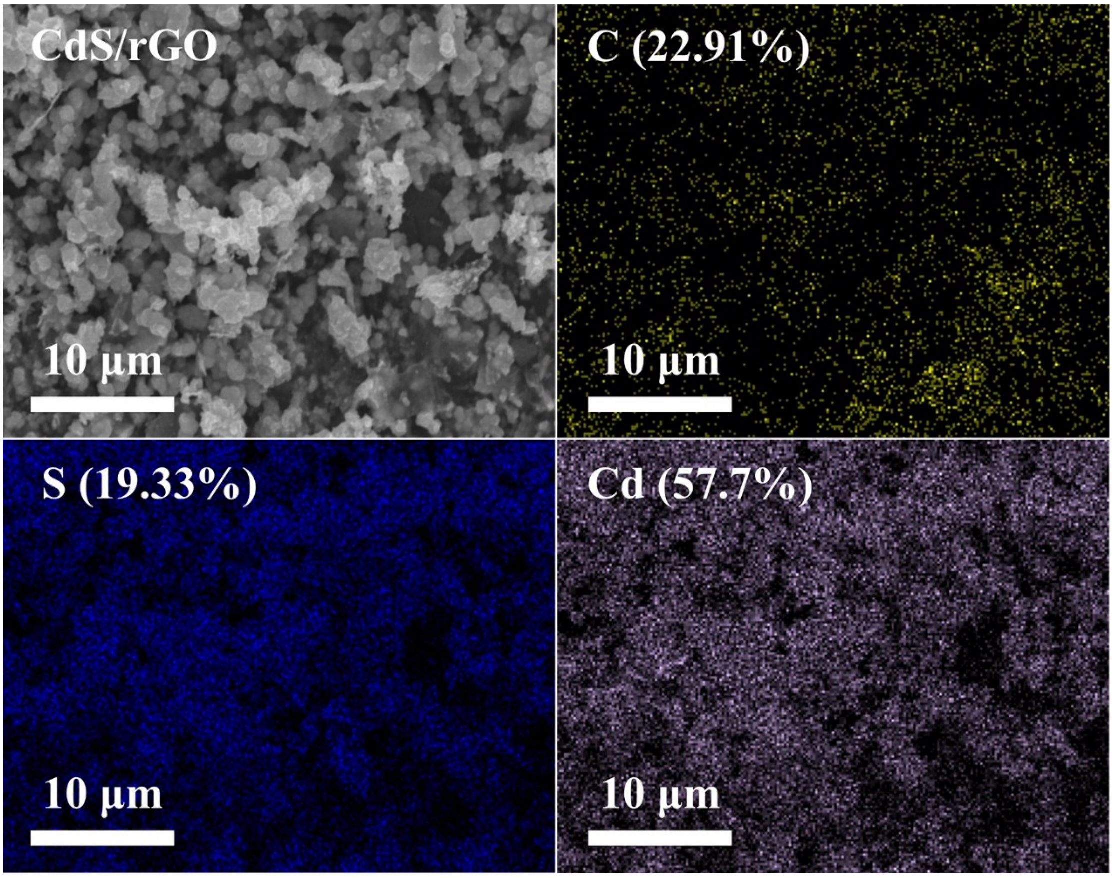

Fig. S9. Energy dispersive X-Ray (EDX) elemental mappings of CdS/rGO.

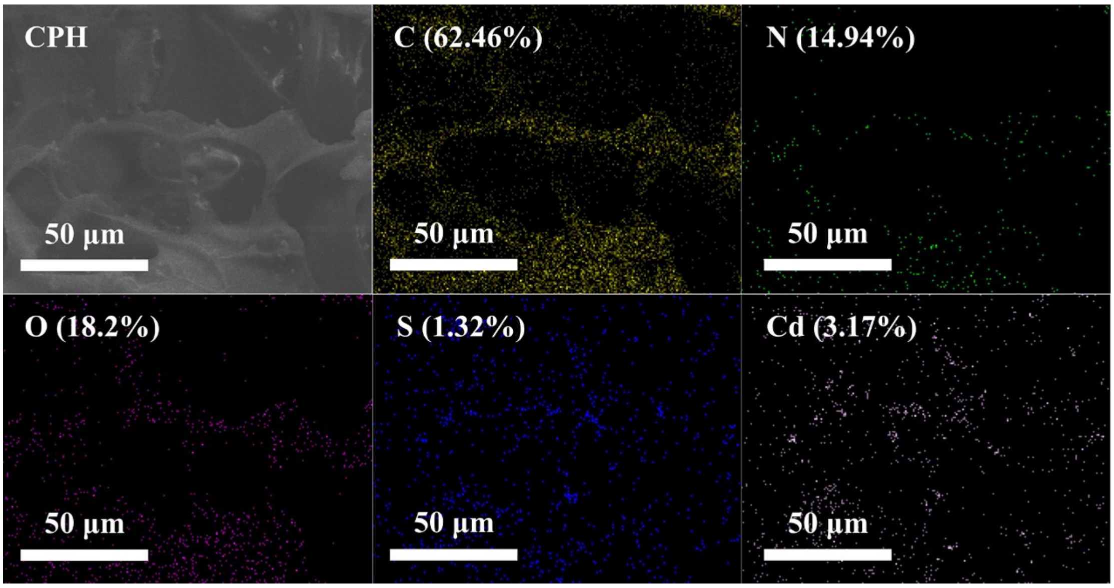

Fig. S10. EDX elemental mappings of CPH.

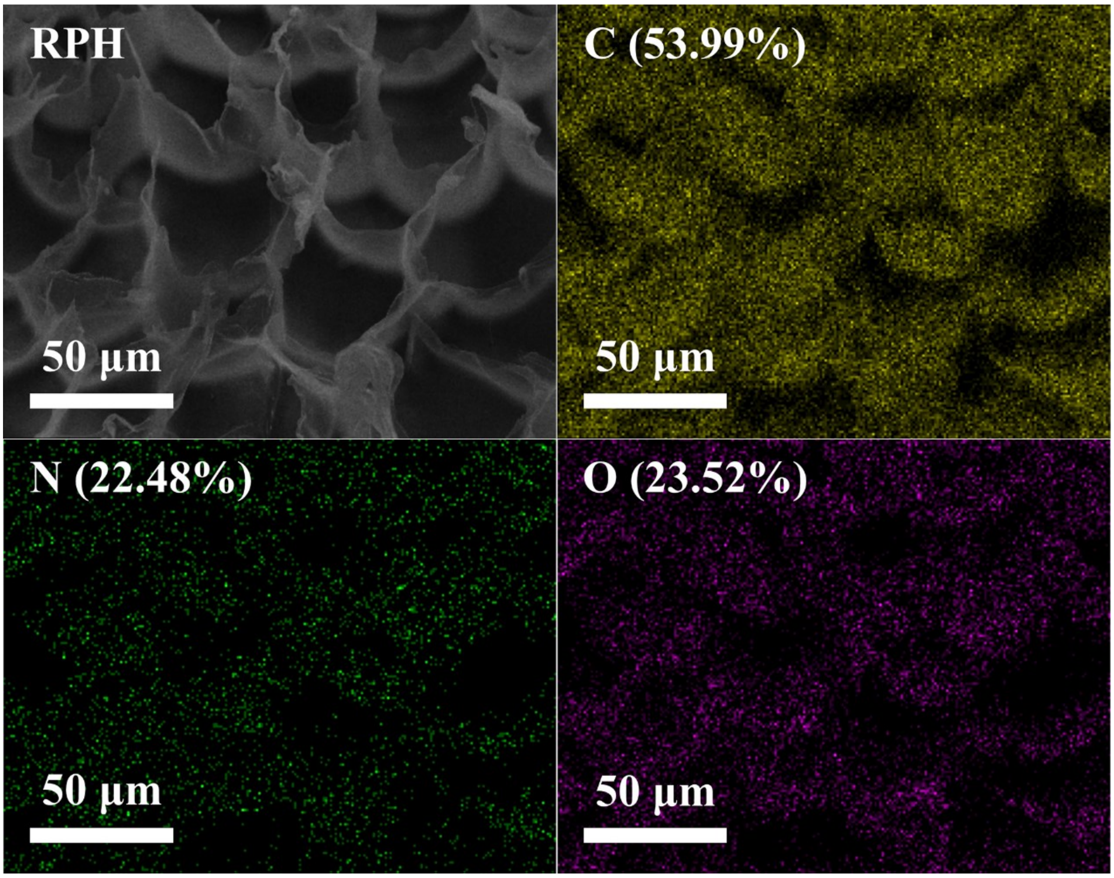

Fig. S11. EDX elemental mappings of RPH.

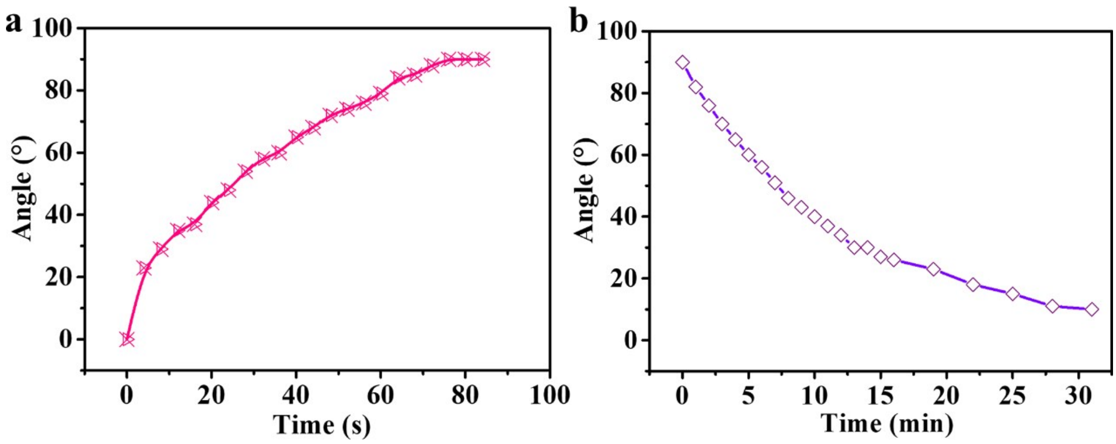

Fig. S12. The time-dependent angle during the processes of (a) bending and (b) recovery of the bionic sunflower.

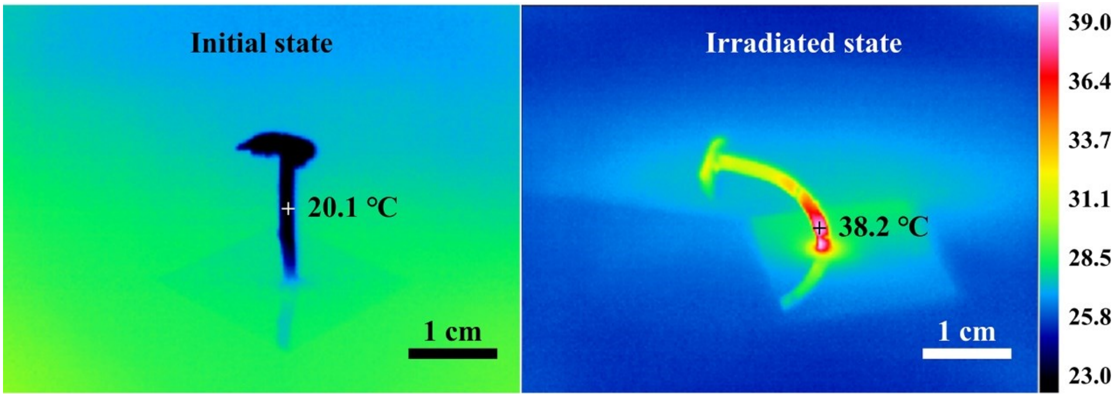

Fig. S13. Infrared images of the bionic sunflower of initial and irradiated states.

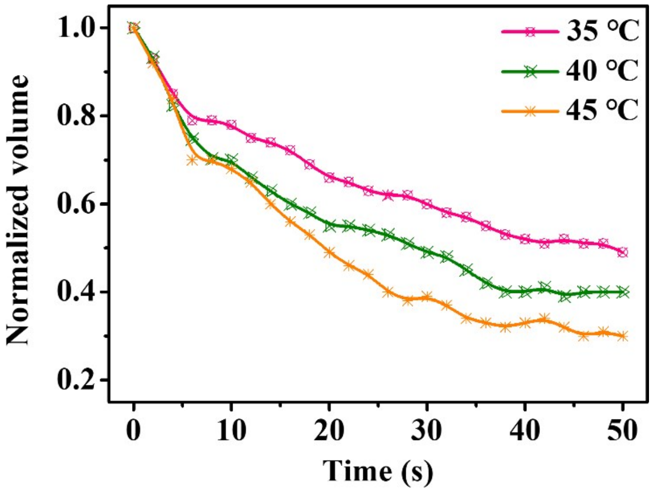

Fig. S14. The curves of shrinking ratios of RPH at different temperatures.

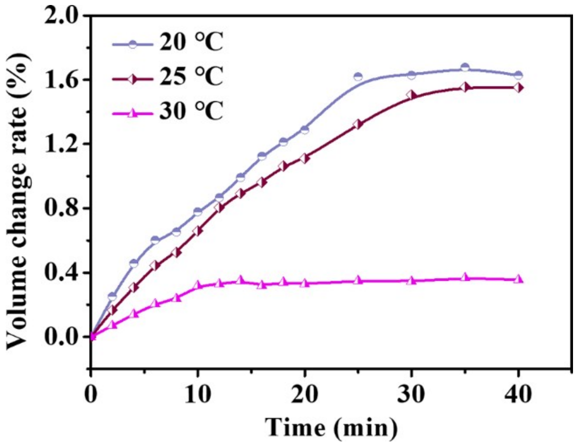

Fig. S15. The curves of volume change rates of dry RPH with time at different temperatures.

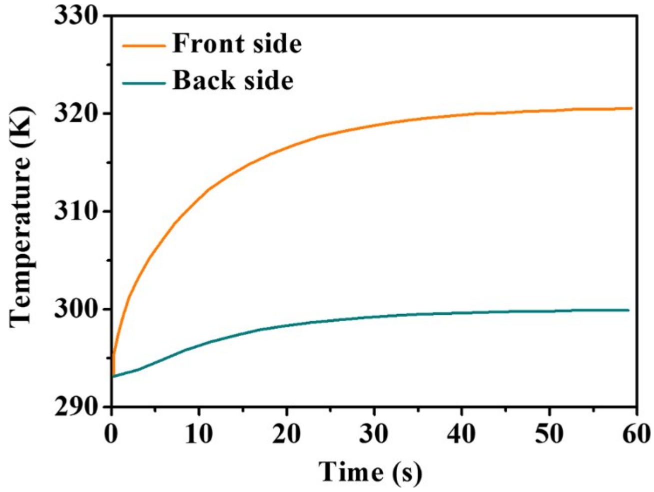

Fig. S16. The time-dependent temperature at different sites of the CPH obtained by simulation results.

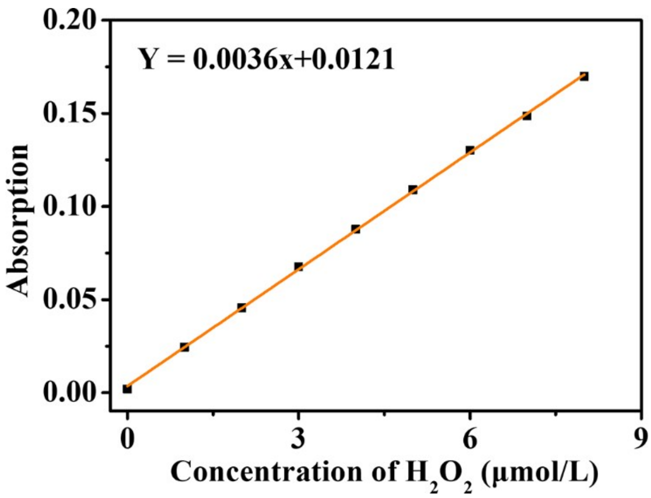

Fig. S17. The linear fitting spectrum of H_2O_2 concentration *vs.* UV-vis absorption intensity ($R^2 = 0.999$).

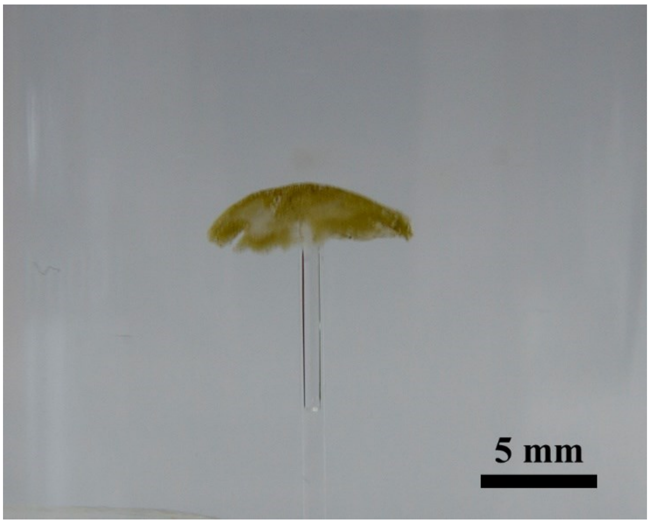

Fig. S18. The photograph of control sample.

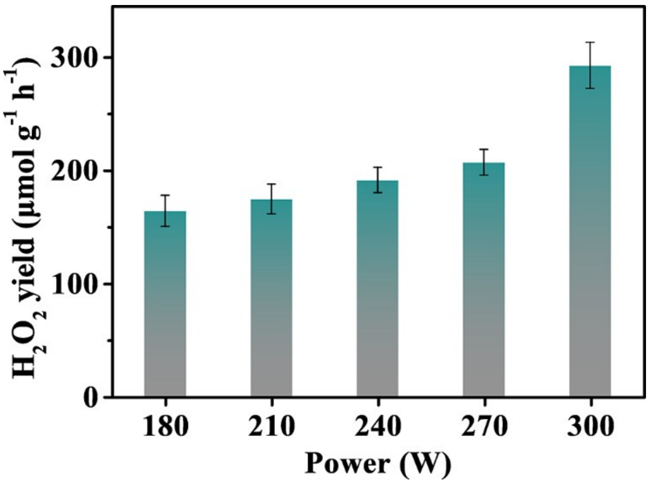

Fig. S19. The H_2O_2 evolution rate of bionic sunflower under different irradiation powers.

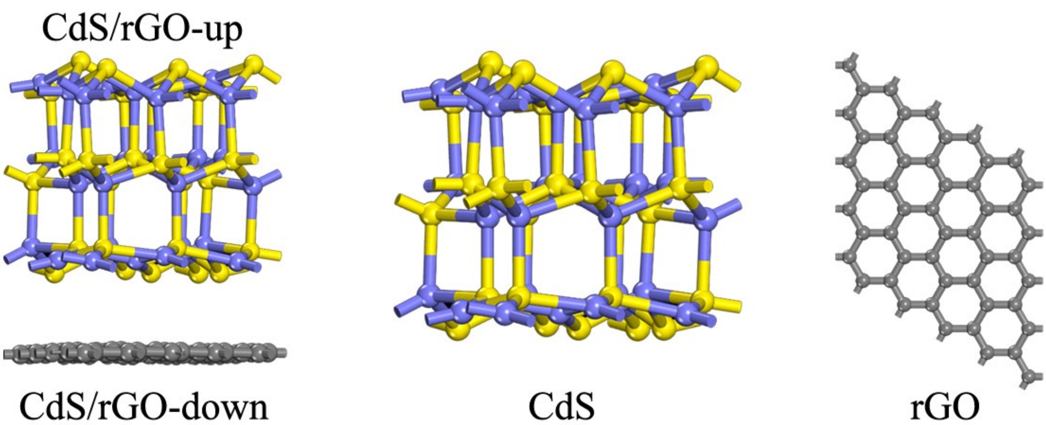

Fig. S20. The optimized atomic models for CdS/rGO, CdS, and rGO.

Table S1. Basic parameters of the material.

Properties		values
Specific heat capacity at constant pressure	C_p	2500 [J/(kg·K)]
Density	ρ	1000 [kg/m^3]
Thermal conductivity	k	0.5 [W/(m·K)]
Heat transfer coefficient	h	420 [W/(m^2·K)]
External temperature	T_{ext}	293.15 [K]

Table S2. The free energies of various states during H_2O_2 formation process.

Free energy (eV)						
	$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2$			**$H_2O + h^+ \rightarrow H_2O_2$**		
States	***OO**	***OOH**	***HOOH**	***H_2O**	***OH**	***HOOH**
CdS	-0.124	0.175	-1.322	-0.389	2.052	2.558
CdS/rGO-up	-0.170	-0.174	-1.396	-0.419	1.945	2.516
CdS/rGO-down	0.169	0.180	-1.053	-0.239	2.249	2.827
rGO	-0.168	0.155	-1.106	-0.239	2.251	2.774

4. Reference

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