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Full-Spectrum Utilization of Solar Energy on Simultaneous CO2 Photoreduction and

Seawater Desalination

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DETAILED SYNTHESIS PROCEDURE

Chemicals and Materials. Aniline monomer ($C_6H_5NH_2$), phytic acid ($C_6H_{18}O_{24}P_6$), copper acetate monohydrate ($Cu(CH_3COO)_2 \cdot H_2O$), sodium borohydride (NaBH₄), and isopropanol ((CH_3)₂CHOH) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Ammonium persulfate ((NH_4)₂S₂O₈) was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd., China. Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) was purchased from Aladdin, China. Carbon paper (H14C9) was purchased from Suzhou Sinero Technology Co., Ltd., China. Nafion PFSA polymer dispersions D520 (5%) was purchased from DuPont de Nemours, Inc. Seawater was obtained from the coast of Qingdao, China, and filtered through a 0.22 µm needle filter before usage. All reagents were used as received without further purification. Ultrapure water (18.2 M Ω), obtained from a DIRECT-Q 5UV purification system (Merck Millipore, Germany), was used in all experiments.

Fabrication of Polyaniline (PANI). 0.458 mL (5 mmol) of aniline monomer was dissolved in 2 mL of deionized water under stirring, then 0.658 mL (1 mmol) of phytic acid was added to the solution. The solution was ultrasonicated to be clear and labeled as solution A. 0.286 g (1.25 mmol) of ammonium persulfate was dissolved in 1 mL of deionized water to prepare solution B. Solution A and B were cooled to 4°C and mixed quickly to obtain PANI hydrogel. Subsequently, immerse the dark green hydrogel in deionized water at a constant temperature of 40°C for 30 minutes for purification, to remove all oligomers and excess ions. Finally, freeze-drying the hydrogel to obtain the powder-like PANI aerogel. Further purification of PANI for photocatalytic CO₂ reduction (CO2R) activity measurement was conducted by several times deionized water washing and freeze-drying in the end.

Fabrication of Oxygen bearing copper (OBCu)-PANI. 20 mg PANI and 80 mg $Cu(CH_3COO)_2 \cdot H_2O$ were dispersed in 50 mL of 75% ethanol-water solution. The mixture was

stirred and ultrasonicated to ensure a homogeneous system. Then, 45.4 mg of NaBH₄ was added dropwise to the mixture. Continuously stir the solution for 3 hours in an ice bath. At last, the product was washed three times with deionized water by centrifugation (8000 rpm, 15 min), and freeze-dried to obtain the products. The samples with different copper concentrations were synthesized as well, using different amounts of copper precursor, noting that NaBH₄ should be 3 times $Cu(CH_3COO)_2 \cdot H_2O$ in moles in every reaction.

Fabrication of OBCu-Oxygen bearing cobalt (OBCo)-PANI. 50 mg OBCu-PANI and 291 mg Co(NO₃)₂•6H₂O were added to 100 mL of deionized water. The mixture was stirred and ultrasonicated to ensure a homogeneous system. Continuously stir the solution for 2 hours under light irradiation of the Xenon lamp. At last, the product was washed three times with deionized water by centrifugation (8000 rpm, 15 min), and freeze-dried to obtain the wanted products.

SUPPLEMENTS ABOUT THE BIFUNCTIONAL CO2R AND WATER EVAPORATION SYSTEM

Loading of catalysts on the carbon paper. First, cut the carbon paper to a size of 2.6 cm*2.6 cm. The square carbon papers were then cleaned by plasma cleaner. 4 mg of the catalyst, 32 μ L of Nafion (5%), and 5 mL of isopropanol were mixed and ultrasonicated for 30 minutes to make a uniform suspension, which was sprayed onto carbon paper. During the spraying, the temperature of the carbon paper was maintained at 50 °C to ensure the evaporation of isopropanol.

Details about the bifunctional reacting system. Figure S1 shows the assembly of the gas diffusion photocatalytic CO2 reduction and seawater desalination system. The reactor consists of one reacting chamber, carbon paper coated with photocatalysts, a flow plate, various types of sealed O-rings, and various parts for fixing and sealing. The volume of the reacting chamber is 5.5 mL. In a typical experiment, saturated K₂CO₃ (aq) was injected into the reacting chamber, and CO₂ gas was fed continuously through the backplate, followed by photocatalytic testing. (In the experiment using seawater, K₂CO₃ was not added.) The outlet gas channel is connected to the condensing equipment, in which the purified water vapor and fuel products are collected under the ice water bath. The light source was a 300 W xenon lamp calibrated to AM 1.5G. The CO₂ gas flow was adjusted to 8 sccm during the reaction. The produced gas-phase products were quantitatively analyzed using an Agilent 8860 gas chromatograph. The sample of the product was injected every 15 minutes. After four hours of reaction, 1 mL of liquid was withdrawn from the reacting chamber and the condensing equipment using a medical syringe, and then a 0.22 µm needle filter was used to prevent bulky obstructions, and the liquid was injected into the liquid chromatography sample bottle. The products were quantitatively analyzed by Agilent 8860 gas chromatography and HPLC-1260 liquid chromatography.



Figure S1. The assembly of the self-made gas diffusion photocatalytic CO_2 reduction and seawater desalination system.

EFFICIENCIES AND SELECTIVITY DETERMINING

Apparent quantum yield (AQY). The quantum yield is calculated by the ratio of the electrons generated by photon excitation and the incident photons, as shown in Equation S1. hc/ λ is the energy of one photon.

$$\phi = \frac{nR_nN_A}{PA/(\frac{hc}{\lambda})}$$

Equation S1

In this equation : ϕ —Apparent quantum yield; *n*—Electrons needed to generate one product molecule; R_n —The generation rate of each kind of products/mol·s⁻¹; N_A —Avogadro constant; *P*—Incident irradiance/W·m⁻²; *A*—Irradiation area/m²; *h*—Planck constant; *c*—The speed of light/m·s⁻¹; λ —The wavelength/m.

Solar to vapor (STV) efficiency.

$$\eta_w = \frac{mE_w}{PA}$$
 Equation S2

In this equation : η_w —STV efficiency; \dot{m} —The mass flux of evaporated water/kg·s⁻¹; E_w —the vaporization enthalpy of the water/J·kg⁻¹; P—Incident irradiance/W·m⁻²; A—Irradiation area/m².

Selectivity to hydrocarbon products. The selectivity is calculated based on the photoelectron distribution.

Selectivity =
$$\frac{nR_n}{\sum n_i R_{ni}}$$
 Equation S3

In this equation : *n*—electrons needed to generate one certain product molecule; R_n —The generation rate of each kind of product/mol·s⁻¹.

SUPPLEMENTS ABOUT THE CHARACTERIZATION OF THE BIFUNCTIONAL HYBRID LIGHT ABSORBER

Morphology of catalysts on carbon paper.



Figure S2. SEM images of OBCu-OBCo-PANI spayed on carbon paper in the view of (a) cross-section and (b)front.



Figure S3. TEM SAED patterns of OBCu-OBCo-PANI.

Figure S4 shows the typical SEM and TEM image of OBCu-OBCo-PANI before and after the reaction. It can be observed that the reaction does not significantly change the morphology.



Figure S4. (a) (b) SEM image of OBCu-OBCo-PANI on carbon paper before and after the reaction. (c) (d) TEM image of OBCu-OBCo-PANI before and after the reaction. (The adhesive substance is Nafion.)



Figure S5. TEM images of OBCu-OBCo-PANI and its elementary mapping.

The Contact angle measurement.



Figure S6. Contact angle measurement of water on carbon paper.

The *Quasi-in-situ* Raman spectroscopy. The assembly of the reactor used for *Quasi-in-situ* Raman spectroscopy is shown in Figure S7. The photocatalysts were sprayed onto carbon paper. Saturated K_2CO_3 (aq) acted as the source of the proton. CO_2 flowed through the back plate. The structure resembles the one in the activity test. The Raman spectra were collected every 5 minutes during the photocatalytic CO2R. The height of the objective table and the position of the glass made only a low-power lens available. The spectrum of higher power lens (100*) was collected by demounting the glass and extracting excessive K_2CO_3 (aq) at the end of CO2R to provide more evident information.



Figure S7. The assembly of the reactor used in the Quasi-in-situ Raman spectroscopy test.



Figure S8. Quasi-in-situ Raman spectra of PANI during CO2R.

Band structure of PANI. The optical bandgap of the semiconductor is calculated by the Tauc plot method.¹ According to Equations S4 and S5, $(\alpha hv)^{1/n}$ and hv can be obtained by manipulating the data of the diffuse reflection spectrum. The $(\alpha hv)^{1/n}$ is plotted against hv, and the straight-line portion in the obtained graph is extended to intersect with the abscissa axis, and the coordinate of the intersection point is the value of the bandgap, which is 3.67 eV for PANI as shown in Figure S9.

$$(\alpha h\nu)^{\frac{1}{n}} = A(h\nu - E_g)$$
 Equation S4

In this equation: α —Absorption coefficient, the ordinate of the diffuse reflection spectrum in this work is the absorption value Abs, which is proportional to α . When using the Abs instead of α in the calculation, the constant A will be changed, while no effect on the determining of the bandgap; *h*—Planck constant, 6.62607015×10⁻³⁴; *v*—Frequency of light/Hz; *n*—Related to semiconductor type. 1/2 for direct bandgap semiconductors and 2 for indirect bandgap semiconductors. 1/2 is adopted in this work; *A*—Constant; *E*_g—Bandgap of semiconductor/eV.

$$v = \frac{c}{\lambda}$$

Equation S5

In this equation: *v*——Frequency of light/Hz; *c*——Speed of light in vacuum, 3×10^8 m/s; λ ——Wavelength of light/m.



Figure S9. Band gaps of PANI, OBCu-PANI, and OBCu-OBCo-PANI calculated by the Tauc plot method.

The valence band spectrum of PANI is shown in Figure S10. The VBM is 3.60 eV below the Fermi level. Meanwhile, according to the Mott-Schottky plot in Figure S11, PANI is an n-type semiconductor and the flat band potential is -0.51 eV vs. Ag/AgCl. Calculated according to Equation S6, the flat band potential is -0.73 eV vs. RHE. The bandgap is 3.67 eV according to the Tauc plot. Thus, the CB of PANI should be located at -0.80 eV vs. RHE, and the VB at 2.87 eV vs. RHE.



$$E_{vs.\,RHE} = E_{vs.\,Ag/AgCl} + 0.197 - 0.059pH$$

Equation S6

Figure S10. The valence band spectrum of PANI.



Figure S11. The Mott-Schottky plot of PANI.

The photoluminescence spectra. Figure S12 shows the photoluminescence spectra of some typical catalysts. It is obvious that after the loading of metal oxides, the recombination of photogenerated carriers is suppressed. The multiple-heterojunction structure enhances charge separation/transport. The intensity is higher with further OBCo loading compared with OBCu-PANI, which may be attributed to increased defects.



Figure S12. The photoluminescence spectra of PANI, OBCu-PANI, and OBCu-OBCo-PANI.

The infrared imaging of photocatalysts.



Figure S13. (a) The infrared imaging of bulk water and PANI on carbon paper before light irradiation, (b) The infrared imaging of bulk water and PANI on carbon paper under light irradiation for 40 min.

The additional information in the FTIR spectra. The peak centered at 1139 cm⁻¹ is related to the plane bending vibration of C–H. The peak centered at 808 cm⁻¹ is due to the para-substitution (p-) of the benzene ring. The unmarked peaks located in the low wavenumber range can be attributed to OBCu and OBCo. Moreover, the peaks at 2849 cm⁻¹, 2924 cm⁻¹, and the band at 3450 cm⁻¹ are due to the stretching vibrations of C–H, N–H, and hydroxyl groups of the adsorbed water, respectively.



Figure S14. FTIR spectra of PANI, OBCu-PANI, and OBCu-OBCo-PANI.

The transmittance of $K_2CO_3(aq)$. The absorption of infrared above 1400 nm is 100% by the potassium carbonate solution as the transmittance value is 0 in Figure S15.



Figure S15. UV-vis spectrum of the potassium carbonate solution.

The change of -NH- revealed by XPS.



Figure S16. (a) XPS spectrum of N 1s line for PANI, (b) XPS spectrum of N 1s line for OBCu-PANI,

The determination of energy flow. The pre-heat of the water body was supported by the transmittance spectrum of K_2CO_3 (aq) in Figure S15. The absorption of infrared above 1400 nm is 100%, besides, the water body was lukewarm after the reaction. The CO₂ reduction (CO2R) reaction was mainly driven by photons with wavelength less than 620 nm, as proved by the AQY test in Figure S16. The part of solar energy put into evaporation (STV efficiency: 71.0%) was higher than the proportion of infrared in the spectrum (< 50%). PANI has better absorption of NIR compared with metal oxide sites as shown in Fig. 5e. Thus, it was a logical deduction that the unused part of UV-vis and NIR would contribute to water evaporation.

SUPPLEMENTS ABOUT THE PERFORMANCE OF CATALYSTS

AQY test. The AQYs of the tandem structure catalyst under different irradiance are shown in Figure S17. Notably, only under the illumination of the 940-nm light source, a 31.5% STV efficiency was gained.



Figure S17. AQYs of the tandem structure catalyst at 365, 410, 620, and 940 nm.

Stability test. The stability test was carried out as shown in Figure S18, 4 hours for every cycle.



Figure S18. Stability test of the tandem structure catalyst.

PANI loaded with different concentrations of OBCu. Figure S19 and S20 shows the CO2R and water evaporation performance of OBCu-PANI with gradient concentrations of OBCu. The number denotes the mass of the copper precursor.



Figure S19. (a) The product yield and (b)selectivity of OBCu-PANI with gradient concentrations of OBCu.



Figure S20. STV efficiency of OBCu-PANI with gradient concentrations of OBCu.

The blank control test of PANI. The experimental settings of the blank control were the same as the former tests (gas diffusion system), except that no CO_2 flow and K_2CO_3 were provided. After 4 hours of irradiation, the color of PANI remained dark green (Figure S21b), rather than purple in the CO2R test (Figure S21a). The product had only HCOOH, and the amount was little as in Figure S21c. Three blank control tests were carried out, one of which yielded nothing. Thus, we believe PANI did not contribute to the products of CO2R.



Figure S21. (a) The digital photo of PANI after the CO2R test. (b) The digital photo of PANI after the blank control test. (c) The contrast of CO2R and blank control tests products using PANI.

PANI in solid-liquid suspension reacting system. Figure S22 shows the CO2R performance of PANI in a solid-liquid suspension reacting system. CO_2 was bubbled into the saturated K_2CO_3 solution during the reaction.



Figure S22. (a) (b) The product yield and selectivity of PANI in a solid-liquid suspension reacting system.

¹³C isotopic tracing of the CO2R. As shown in Figures S23 and S24, The TIC has the typical peaks of CO and C_3H_7OH . Further analysis of the extracted mass spectrum confirms the existence of ${}^{13}C_3H_7OH$ as the reduction product of ${}^{13}CO_2$.



Figure S23. TIC scan of ¹³C isotopic tracing (gas-phase products).



Figure S24. Analytic data of ¹³C isotopic tracing. (a) TIC scan, (b) ¹³C mass spectrum. (liquid-phase products)

Inductively Coupled Plasma Mass Spectrometer results.

Sample	The concentration of K ⁺ (µg/mL)	
The liquid in the reactor	469	
The liquid in the condensing equipment	0.413	

Table S1. The ion concentration after water evaporation

 Table S2. The result of seawater desalination.

Sample	The concentration of K ⁺ (mg/mL)	The concentration of Mg ²⁺ (mg/mL)	The concentration of Ca ²⁺ (mg/mL)	The concentration of Na ⁺ (mg/mL)
Original seawater	0.359	1.13	0.293	8.82
The liquid in the reactor after the reaction	0.401	1.35	0.289	10.3
The liquid in the condensing equipment	0.088	0.1275	0.0334	0.941

DETAILS ABOUT DFT CALCULATION

In determining the reaction energy, we factored in frequency correction. The free energy change (ΔG) of each step could be calculated as

$$\Delta G = \Delta E + \Delta \int C_p dT - T\Delta S + \Delta ZPE$$
 Equation S7

where ΔE is the energy change calculated by DFT, $\Delta \int C_p dT$ is the enthalpy change, T is the temperature and ΔS is the entropy change. ΔZPE is the zero point energy (ZPE) change. All the temperature was set to 298.15K. All thermal correction was processed by VASPKIT software².

For the building of the two main surface models shown in Figure S25, first, we verified the reaction sites through *quasi-in-situ* Raman spectroscopy to be Cu/Co. While the concentration of Cu₂O exceeded Co₃O₄ in our samples. Therefore, the DFT model used Cu₂O as the base and carried PANI and Co₃O₄ on it. For PANI, the previous research has proved that its redox characteristics are mainly reflected at the N atoms at both ends of the benzene ring,³ so we intercepted a single benzene ring, retained the redox end rather than using the long-chain structure (Figure S25a). When building Co₃O₄ clusters, we ensured the stoichiometric ratio of Co₃O₄ (Figure S25b).



Figure S25. The structure of Cu₂O-PANI (a) and Cu₂O-Co₃O₄-PANI(b).



Figure S26. The structure of H_2O absorbed on and catalytic surface.



Figure S27. The structure of *CO absorbed on Co_3O_4 cluster(a) and $Cu_2O(b)$. The numbers in the diagram represent the adsorption energy values.

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