*Supporting Information*

**A light-****management film layer induces** **dramatically enhanced acetate production in photo-assisted microbial electrosynthesis systems**

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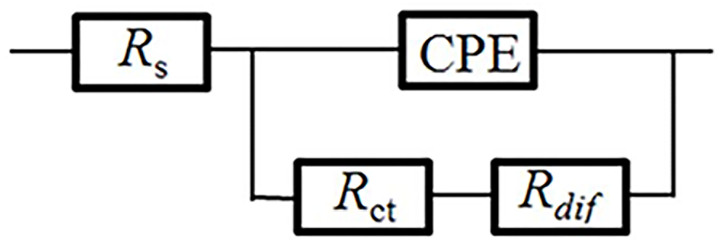
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**S2 Materials and methods**

*S2.1 Synthesis of MnFe2O4/AZO and MnFe2O4/ g-C3N4/AZO photocathodes*

Pure g-C3N4 was synthesized by heating melamine (99.8%) at 550 °C for 2 h in muffle furnace. This g-C3N4 was added into 50 mL deionized water and ultrasonicated for 1 h. 0.132 g MnCl2⋅4H2O, 0.301 g FeCl3.6H2O and 0.164 g urea were dissolved into the above solution with 0.5 h magnetic stirring. Then the pH was adjusted to 12 using 5 M NaOH while stirring further for 1 h. After that, the solution was transferred to a 100 mL Teflon autoclave, heated at 200 °C for 8 h to prepare the MnFe2O4/g-C3N4 photocatalyst. The as-prepared photocatalyst was added into the aged sol with a molar ratio at 1:3 and ultrasonicated for 1 h, dried at 80 °C for 12 h. Thereafter, the mixture was finally annealed at 400 ℃ for 1 h to obtain MnFe2O4/g-C3N4/AZO in powder form.

1.5 g of the MnFe2O4/g-C3N4/AZO powder was dispersed in 1 L deionized water and ultrasonicated for 10 h. The supernatant was attained by centrifuging the above suspension for 10 min at 5000 r/min, and then 2.0 × 2.0 × 0.25 cm graphite felts (Sanye Co., Beijing, China) were immersed in the supernatant overnight and dried at 60 ℃ for 12 h to obtain the MnFe2O4/g-C3N4/AZO cathodes. Finally, the cathodes were calcined at 300 °C for 2 h in muffle furnace with a heating rate of 2 °C /min. The MnFe2O4/AZO cathode was fabricated by the same procedures except the addition of g-C3N4.

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*R*s: A series resistance for ohmic transport in the electrolyte and other contact effects;

*R*ct: charge transfer resistance;

*R*dif: diffusion resistance;

CPE: constant phase elecment.

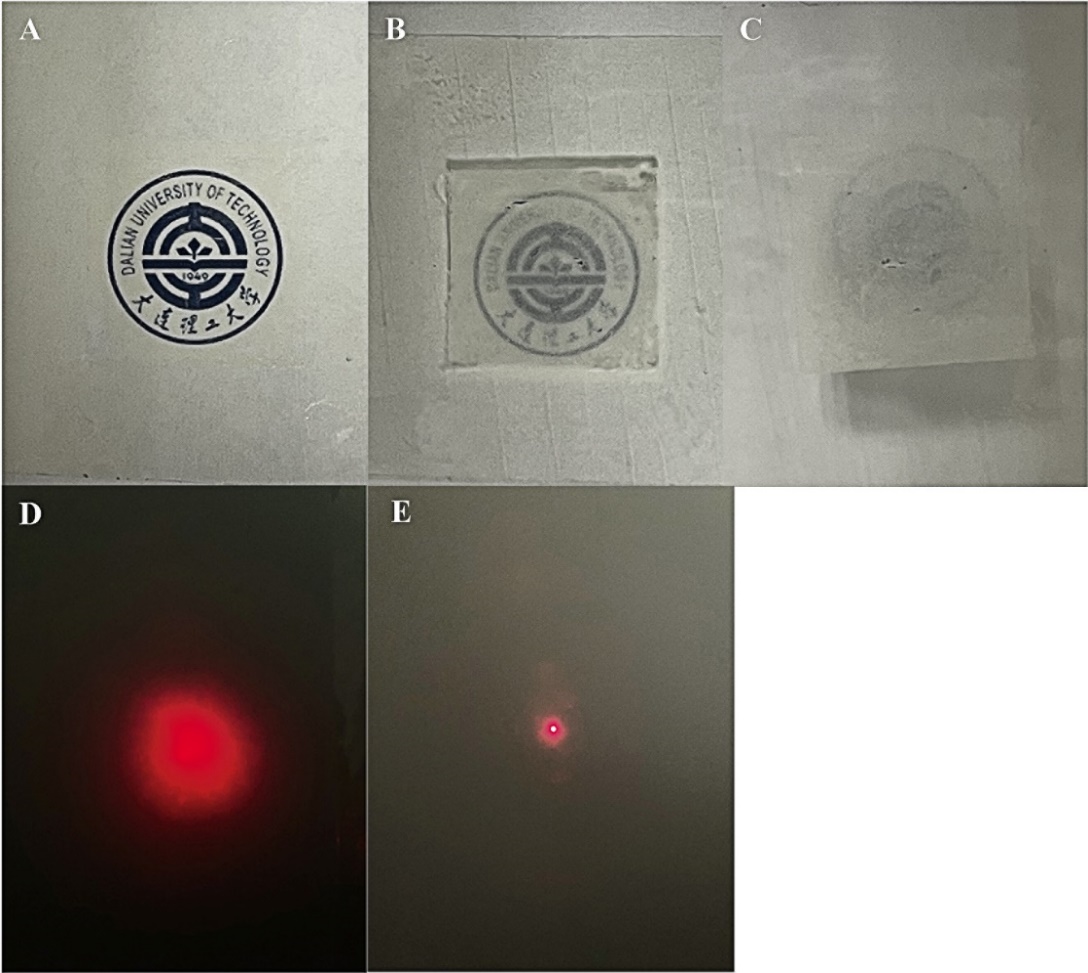
**Fig. S1** Equivalent circuits of the EIS Nyquist plots.



**Fig. S2** Radiation spectrum of the lamp.



**Fig. S3** The schematic diagram of the photo-assisted MES.



**Fig. S4** Photographs show the printed image as seen through the AZO film, while the film is placed apart from the image by a distance of 0 cm (A), 1 cm (B), and 3 cm (C). Visual images of light scattering effect by a red laser for the AZO film (D) and glass substrate (E).



**Fig. S5** Mott-Schottky plots of g-C3N4/AZO (A), AZO (B) and g-C3N4 (C).



**Fig. S6** Photoluminescence spectra under 400 nm excitation of various photocatalysts.



**Fig. S7** The schematic diagram of transient photocurrent response and light reflecting behaviors of g-C3N4/AZO (A), AZO (B) and g-C3N4 (C) by UV-vis incident light with different incident angles.



**Fig. S8** Element mapping images of g-C3N4/AZO.



**Fig. S9** Flow cytometry analysis of live/dead electrotrophs on the photocathodes of g-C3N4/AZO (A), AZO (B) and g-C3N4 (C). The controls of electrotrophs without propidium iodide staining (D).



**Fig. S10** High resolution XPS spectra of g-C3N4/AZO, AZO or g-C3N4.



**Fig. S11** Acetate production (A), residual H2 (B), *CE*acetate (C) and inorganic carbon consumption (D) for g-C3N4/AZO at different ratios.



**Fig. S12** Acetate production (A), residual H2 (B), *CE*acetate (C) and inorganic carbon consumption (D) for g-C3N4/AZO at different dip-coating cycles.



**Fig. S13** Acetate production (A), residual H2 (B), *CE*acetate (C) and inorganic carbon consumption (D) for g-C3N4/AZO with different OD600.



**Fig. S14** Acetate production (A), residual H2 (B), *CE*acetate (C) and solar-to-acetate efficiency (D) of various photocathodes at different cathode potentials with 400 nm UV-cut filters.



**Fig. S15** Time course of acetate production (A), residual H2 (B), *CE*acetate (C), inorganic carbon consumption (D) and Nyquist plots of EIS spectra (E and F) for different cathodes (operational time: 2.5 d).



**Fig. S16** Nyquist plots of EIS spectra (A) and residual inorganic carbon (B) for different cathodes over a 12 day operation with periodical addition of bicarbonate. SEM image (C) and EDS spectrum (D) of g-C3N4/AZO bio-photocathode at the end of the 12 days operation.



**Fig. S17** XRD patterns of the g-C3N4/AZO photocathode before and after DPV.

**Table S1** EIS parameters obtained from Nyquist plots and DPV data of various cathodes.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  | | EIS | | | | | |  | |  | | DPV | | | | | | | |
|  | | *R*s (Ω) | | *R*ct (Ω) | | *R*dif (Ω) | |  | |  | | *E*p-acetate (V) | | *I*p-acetate (mA) | | *E*p-cytochrome c (V) | | *I*p-cytochrome c (mA) | |
| g-C₃N₄/AZO | |  | | 12.1 | | 48 | | 36.6 | |  | |  | | -0.51 | | -2.57 | | 0.028 | | -0.76 | |
| g-C₃N₄/AZO-filter | |  | | 12.1 | | 70 | | 36.8 | |  | |  | | -0.53 | | -2.12 | | 0.026 | | -0.62 | |
| g-C₃N₄/AZO-no light | |  | | 12.6 | | 76 | | 37.2 | |  | |  | | -0.60 | | -1.92 | | 0.012 | | -0.50 | |
| g-C₃N₄/AZO-abiotic | |  | | 11.3 | | 88 | | 37.5 | |  | |  | | --- | | --- | | --- | | --- | |
| AZO | |  | | 11.8 | | 94 | | 36.4 | |  | |  | | -0.55 | | -1.63 | | 0.024 | | -0.52 | |
| g-C₃N₄-filter | |  | | 13.5 | | 104 | | 37.1 | |  | |  | | -0.55 | | -1.58 | | 0.022 | | -0.48 | |
| Bare glass | |  | | 10.3 | | 153 | | 38.5 | |  | |  | | -0.56 | | -0.93 | | 0.020 | | -0.35 | |

**Table S2** Comparison of EIS parameters obtained from Nyquist plots as a function of operational time.

|  |  |  |  |
| --- | --- | --- | --- |
|  | *R*s (Ω) | *R*ct (Ω) | *R*dif (Ω) |
| g-C₃N₄/AZO-0.5 d | 12.2 | 49 | 37 |
| g-C₃N₄/AZO-1.0 d | 12.2 | 49 | 50 |
| g-C₃N₄/AZO-1.5 d | 12.3 | 49 | 928 |
| g-C₃N₄/AZO-2.0 d | 12.3 | 49 | 1248 |
| g-C₃N₄/AZO-2.5 d | 12.4 | 50 | 2034 |
| g-C₃N₄/AZO-filter-0.5 d | 12.1 | 70 | 37 |
| g-C₃N₄/AZO-filter-1.5 d | 12.3 | 71 | 64 |
| g-C₃N₄/AZO-no light-0.5 d | 12.7 | 76 | 37 |
| g-C₃N₄/AZO-no light-1.5 d | 12.7 | 76 | 51 |
| AZO-0.5d | 11.8 | 94 | 37 |
| AZO-1.5d | 11.9 | 95 | 47 |
| g-C₃N₄-filter-0.5d | 13.5 | 109 | 38 |
| g-C₃N₄-filter-1.5d | 13.6 | 120 | 44 |
| Bare glass-0.5d | 10.4 | 153 | 39 |
| Bare glass-1.5d | 10.5 | 153 | 41 |

**Table S3** Comparison of EIS parameters obtained from Nyquist plots of different cathodes with interval supplementary bicarbonate.

|  |  |  |  |
| --- | --- | --- | --- |
|  | *R*s (Ω) | *R*ct (Ω) | *R*dif (Ω) |
| g-C₃N₄/AZO-0.5 d | 12.2 | 49 | 37 |
| g-C₃N₄/AZO-6 d | 12.5 | 49 | 39 |
| g-C₃N₄/AZO-12 d | 12.7 | 50 | 38 |
| g-C₃N₄/AZO-filter-0.5 d | 12.1 | 70 | 37 |
| g-C₃N₄/AZO-filter-6 d | 12.5 | 71 | 39 |
| g-C₃N₄/AZO-filter-12 d | 12.8 | 72 | 38 |
| g-C₃N₄/AZO-no light-0.5 d | 12.7 | 76 | 37 |
| g-C₃N₄/AZO-no light-6 d | 12.8 | 77 | 37 |
| g-C₃N₄/AZO-no light-12 d | 12.9 | 77 | 38 |
| AZO-0.5d | 11.8 | 94 | 37 |
| AZO-6 d | 12.0 | 96 | 38 |
| AZO-12 d | 12.4 | 96 | 37 |
| g-C₃N₄-filter-0.5d | 13.5 | 109 | 38 |
| g-C₃N₄-filter-6 d | 13.6 | 131 | 38 |
| g-C₃N₄-filter-12 d | 13.2 | 142 | 37 |
| Bare glass-0.5d | 10.4 | 153 | 39 |
| Bare glass-6 d | 11.0 | 153 | 37 |
| Bare glass-12 d | 11.3 | 154 | 38 |