

Supporting Information

Construction of a metal-free photocatalyst via encapsulation of 1,2,3,5-tetrakis(carbazole-9-yl)-4,6-dicyanobenzene in carboxymethylcellulose-based hydrogel for photocatalytic lactic acid production

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Experimental section

Materials and reagents

Carboxymethylcellulose (CMC), acrylic acid (AA, >99.0%), 2-hydroxyethyl acrylate (HEA, 97.0%), 1,2,3,5-tetrakis(carbazole-9-yl)-4,6-dicyanobenzene (4CzIPN, 98.0%), *N,N'*-methylenebisacrylamide (99.0%), and ammonium persulfate (98.5%) were provided by Sinopharm Chemical Reagent Co., Ltd. Xylose ($\geq 99.0\%$), arabinose ($\geq 99.0\%$), fructose (99.0%), glucose (99.0%), mannose (99.0%), rhamnose (99.0%), potassium iodide (KI, $\geq 99.5\%$), tryptophan (Trp, 98.0%), benzoquinone (BQ, 99.0%), *p*-phthalic acid (PTA, 99.0%) and potassium hydroxide (KOH) were purchased from Aladdin Chemistry Co. (Shanghai, China). All the used chemicals were used as received without further purification.

Recycling tests

To investigate the stability and reusability of the 4CzIPN@CMC-HG photocatalyst, a series of recycling tests were carried out. Typically, a mixture of xylose (0.1 g), 4CzIPN@CMC-HG (0.5 g), and KOH solution (10.0 mL, 8.0 M) was stirred in the dark for 30 min. Subsequently, the reaction system was performed at 50 °C for 140 min via visible light irradiation. Following, the photocatalyst was filtered and washed with deionized water for reuse. Meanwhile, the collected filtrate was analyzed using HPLC.

One-thousand-fold scale-up experiments

To study the industrial application potential of this photocatalytic system, a one-thousand-fold scale-up experiment was carried out. Here, the light source and reaction temperature were changed to sunlight and room temperature. For this reaction, 100.0 g of xylose and 500.0 g of 4CzIPN@CMC-HG were added into 10.0 L KOH solution with concentration of 2.0 M. The obtained system was first stirred in the dark for 30 min, and then conducted at room temperature (~ 25 °C) for 140 min in the presence of sunlight irradiation. After the reaction, the conversion of xylose and the yields of products or by-products were analyzed by HPLC.

The trapping experiments of active oxidation species

To investigate the roles of different active oxidation species (e.g., h^+ , $\cdot OH$, $\cdot O_2^-$, and 1O_2) on the LA yields photocatalyzed by 4CzIPN@CMC-HG, a series of trapping experiments were conducted. Typically, a mixture of xylose (0.1 g), 4CzIPN@CMC-HG (0.5 g), and sacrificial agents (0.125 mM, *p*-phthalic acid (PTA), potassium iodide (KI), tryptophan (Trp), and

benzoquinone (BQ)) was added into KOH solution (10.0 mL, 8.0 M). The generated reaction systems were stirred for 30 min under the dark condition and then irradiated by visible light at 50 °C for 140 min. Finally, the liquid products were studied using HPLC.

Characterizations

The morphology and structure of the 4CzIPN@CMC-HG and CMC-HG photocatalysts were investigated by scanning electron microscope (SEM, JSM-7800F), Fourier transform infrared spectroscopy (FT-IR, Nicolet Nexus 470), X-ray diffraction patterns (XRD, Bruker D8 Advance diffractometer), X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI) according to a previous report.¹ The ultraviolet-visible diffuse reflectance spectra (UV-vis DRS), ultraviolet photoelectron spectroscopy (UPS), and electron spin-resonance (ESR) spectroscopy of the 4CzIPN@CMC-HG and CMC-HG were recorded and analyzed based on the method described by Ma et al..² Additionally, the electrochemical impedance spectra (EIS), Mott-Schottky plot, and transient photocurrent response (I-t) were all performed in the electrolyte of Na₂SO₄ (0.5 M) with a three-electrode electrochemical cell.³

Calculation of the work function and valence band

The work functions (φ) and the valence band potential (E_{VB}) of the samples were calculated according to the following equations:

$$\varphi = h\nu - E_{cutoff} \quad \text{Eq. S1}$$

$$E_{VB} = \varphi + E_{edge} \quad \text{Eq. S2}$$

Where $h\nu$ is the photo energy of excitation light (He I discharge lamp, 21.2 eV), E_{cutoff} is the high binding energy cutoff edge, and E_{edge} is the low binding energy cutoff edge.

Results and discussion

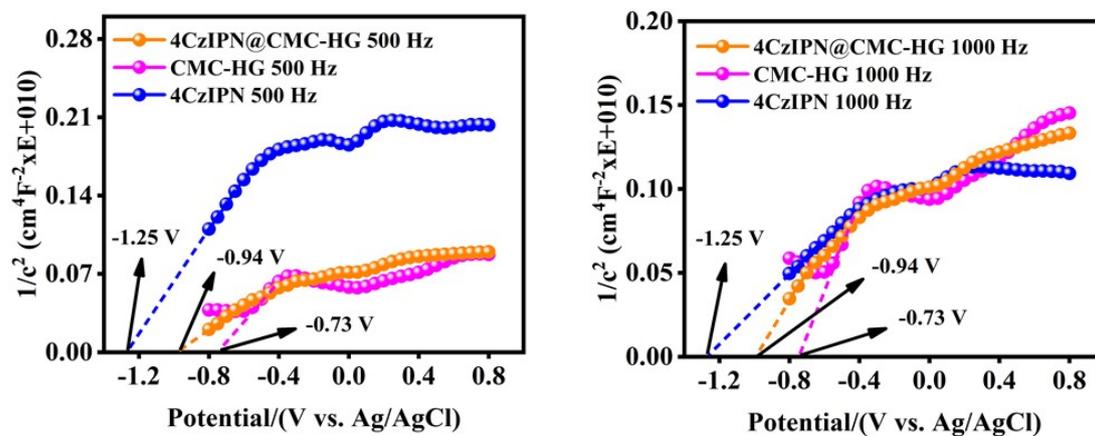


Fig. S1 Mott-Schottky plots of the 4CzIPN@CMC-HG, CMC-HG, and 4CzIPN at frequencies of 500 Hz and 1000 Hz.

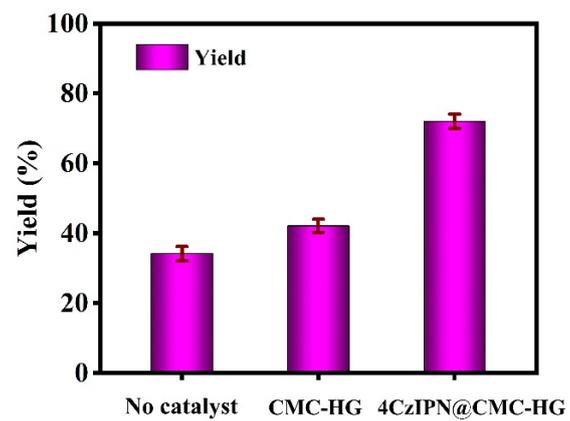


Fig. S2 The effects of no catalyst, CMC-HG, and 4CzIPN@CMC-HG on the yield of LA under the dosage of 0.5 g catalyst.

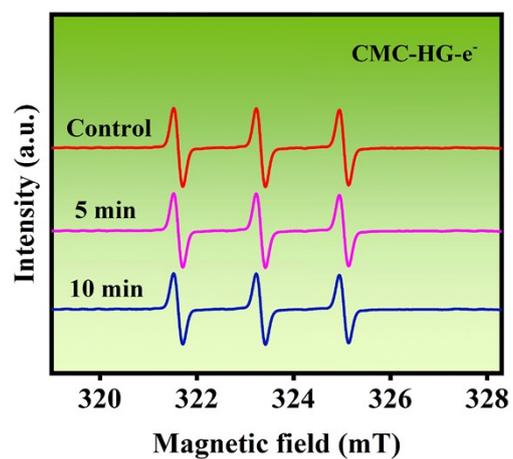


Fig. S3 TEMPO ESR spin-labeling for e⁻ of the CMC-HG (Control: under the dark conditions of irradiation without spin-labeling, 5 min: irradiation for 5 min, 10 min: irradiation for 10 min).

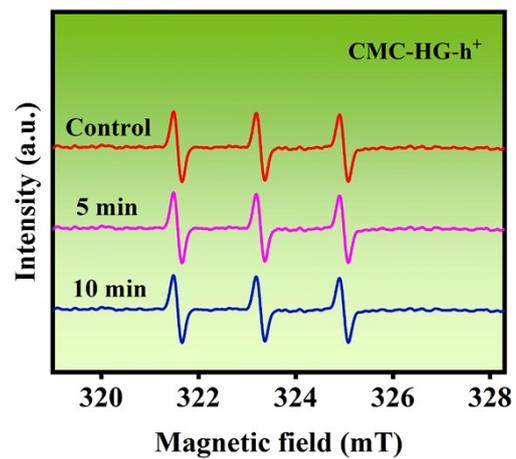


Fig. S4 TEMPO ESR spin-labeling for h⁺ of the CMC-HG.

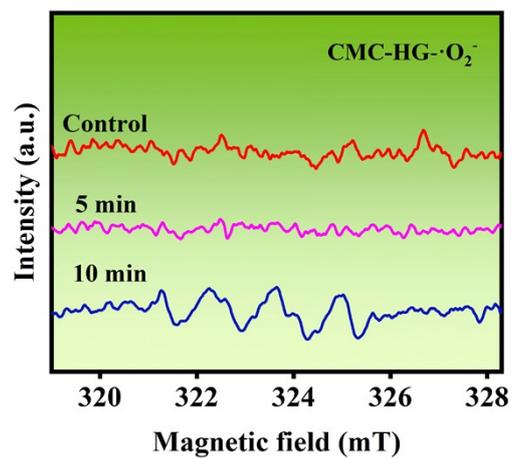


Fig. S5 DMPO ESR spin-labeling for $\cdot\text{O}_2^-$ of the CMC-HG.

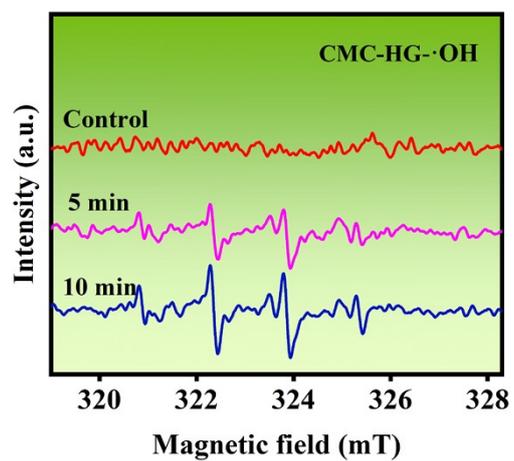


Fig. S6 DMPO ESR spin-labeling for $\cdot\text{OH}$ of the CMC-HG.

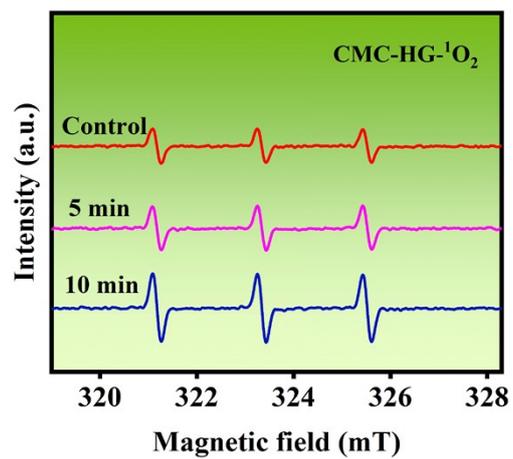


Fig. S7 TEMPONE ESR spin-labeling for ¹O₂ of the CMC-HG.

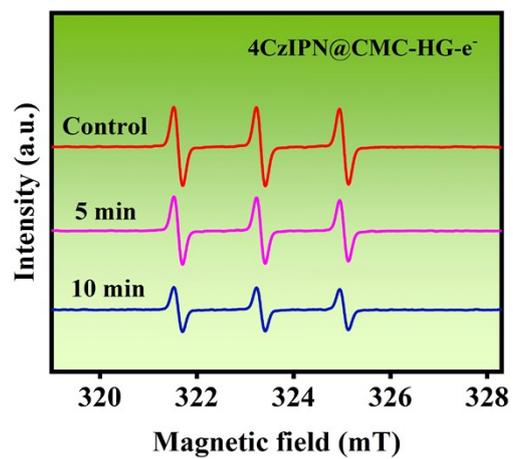


Fig. S8 TEMPO ESR spin-labeling for e⁻ of the 4CzIPN@CMC-HG.

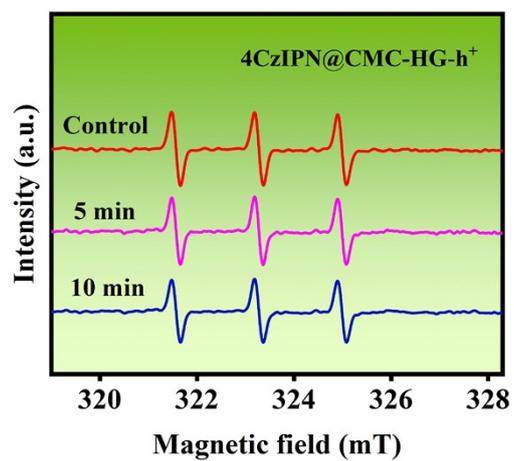


Fig. S9 TEMPO ESR spin-labeling for h⁺ of the 4CzIPN@CMC-HG.

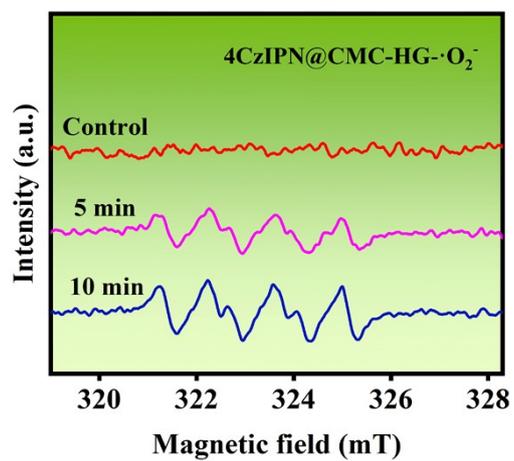


Fig. S10 DMPO ESR spin-labeling for $\cdot\text{O}_2^-$ of the 4CzIPN@CMC-HG.

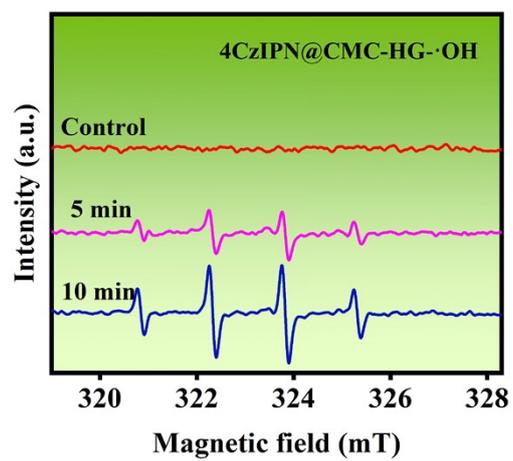


Fig. S11 DMPO ESR spin-labeling for $\cdot\text{OH}$ of the 4CzIPN@CMC-HG.

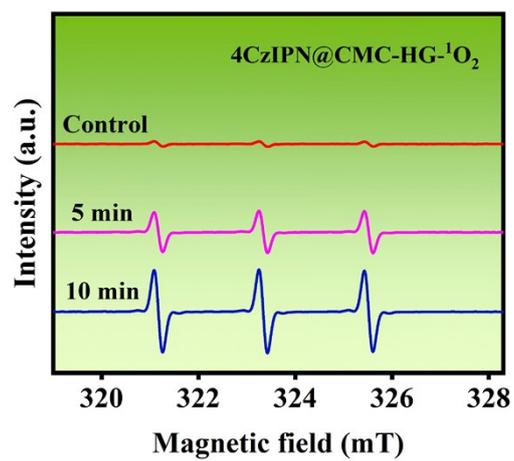


Fig. S12 TEMPONE ESR spin-labeling for ¹O₂ of the 4CzIPN@CMC-HG.

References

- 1 J. L. Ma, Y. C. Li, D. N. Jin, Z. Ali, G. J. Jiao, J. Q. Zhang, S. Wang and R. C. Sun, *Green Chem.*, 2020, **22**, 6384-6392.
- 2 J. L. Ma, D. N. Jin, Y. C. Li, D. Q. Xiao, G. J. Jiao, Q. Liu, Y. Z. Guo, L. P. Xiao, X. H. Chen, X. Z. Li, J. H. Zhou and R. C. Sun, *Appl. Catal. B: Environ.*, 2021, **283**, 119520.
- 3 L. X. Chen, T. Liu and D. B. Chao, *Chem. Eng. J.*, 2022, **429**, 132348.