Supporting Information

One-Pot Sequential Cascade Reaction for Selective Gluconic Acid Production from Cellulose Photobiorefining

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Experimental Section

Synthesis of MCN and AKCN. Typically, 1.5 g melamine, 80 mmol potassium chloride and 2 mmol potassium hydroxide were mixed thoroughly to obtain homogeneous mixture in a mortar. Then the mixture was placed in a 100 mL crucible with a lid and heated at 550 °C for 4 hours with a heating rate of 2.2 °C per minute under air atmosphere. Subsequently, the obtained solid sample was gently grounded and placed in deionized water under ultrasonication for 3 h. After that, the powder was completely washed and centrifuged several times to remove the soluble substance, and then dried at 70 °C overnight. Ultimately, the resulting powers were marked as AKCN. For comparison, MCN was synthesized by one-step calcination process of melamine as the precursor without the addition of potassium chloride and potassium hydroxide. 1.5 g melamine was calcined at 550 °C for 4 hours with a heating rate of 2.2 °C per minute under air atmosphere. The final powers were labelled as MCN.

Synthesis of cellulose-II. The commercial Avicel was adopted to obtain the type-II cellulose under alkali pretreatment. In detail, 1g Avicel powders was mixed with 5 M sodium hydroxide solution under continuous stirring for 2 hours. Then the powders were washed with deionized water until the supernatant is neutral, followed by removing the solution and drying at 70 °C overnight for further tests. The resultant white powders were named as cellulose-II.

Characterizations. The XRD patterns were characterized by a Bruker D8 Advance instrument with Cu-Kα as the radiation source. The FTIR spectra were analyzed by a Thermo Scientific Nicolet iS 50 FT-IR spectrometer. UV-visible DRS were conducted

on a UV-visible spectrometer (Lambda, PerkinElmer). Photoluminescence (PL) emission spectra were measured on a Fluorescence Spectrophotometer (F-4700, Hitachi, Japan). TRPL spectra were characterized on a FLS920 fluorescence lifetime spectrophotometer (Edinburgh Instruments, UK) with an excited wavelength at 350 nm. XPS was used to investigate the chemical states of the samples (Escalab, 250Xi, Thermo Scientific). The C 1s peak of adventitious carbon at 284.8 eV was used to calibrate the binding energies. Field emission scanning electron microscope (FESEM, JSM 7500F) and high-revolution transmission electron microscope (HRTEM, Talos 200) were adopted to observe the morphology of the samples. The electrochemical measurements were tested on a CHI660D workstation. The working electrode, reference electrode and counter electrode were corresponding to an FTO glass loaded with samples, Ag/AgCl electrode and Pt, respectively, which were placed in 0.1 M Na_2SO_4 aqueous solution. The ESR spectra were measured via ESR spectrometer (JES-X320, JEOL).

Photocatalytic measurement. A glass vial with a total volume of 20 mL was adopted for the photocatalytic tests. Typically, 2g/L concentration of glucose solution with 10 mL volume was prepared and 10 mg of the photocatalyst was dispersed uniformly in the above solution. The reactor was tightly sealed and placed in dark condition for 1-h constant stirring. A Xenon lamp with the power of 300W was then utilized to initialize the photocatalytic reaction. The glucose and other reaction products were detected by high-performance liquid chromatography (HPLC, 1200 Agilent system) with a Aminex HPX-87H column (300 * 7.8 mm, Bio-Rad) and a refractive index detector (RID). The

mobile phase was 5 mM sulfuric acid at the flow rate of 0.6 mL/min. In addition, error bar was obtained by repeating each experiment for three times. The glucose conversion, gluconic acid selectivity and gluconic acid yield are calculated as below:

$$\text{Glucose conversion} = \frac{[\text{glucose}]_O - [\text{glucose}]_T}{[\text{glucose}]_O} \times 100\ \%$$

$$\text{Gluconic acid selectivity} = \frac{[\text{gluconic } acid]_T}{[\text{glucose}]_O - [\text{glucose}]_T} \times 100\ \%$$

$$\text{Gluconic acid yield} = \frac{[gluconic\ acid]_T}{[\text{glucose}]_O} \times 100\ \%$$

$[glucose]_O$ and $[glucose]_T$ are corresponding to the molar concentration of original glucose solution and the exact time T during the reaction. $[\text{gluconic acid}]_T$ represents the molar concentration of gluconic acid at the exact time T during the reaction.

Photobiocatalytic measurements. Typically, 1g/L cellulose-II was thoroughly mixed with 10 mL of 50 mM acetic buffer solution (pH=5.2) and 5 mg of the photocatalyst was dispersed uniformly in the above solution. Then, 20 μL cellulase enzymes was added into the dispersion before 8-h photobiocatalytic reaction under 50 ℃. After the reaction finished, 10 μL cellulase enzymes was added into the reactor to completely hydrolyze the residue cellulose for 72 h under 50 ℃. The cellulase enzymes carried out in the reactions are Novozyme CTec2.[1-3]

$$\text{Cellulose conversion} = [1 - \left(\frac{[\text{glucose}]_{72} - [\text{glucose}]_8}{1.11}\right)] \times 100\ \%$$

$$\text{Glucose conversion} = \frac{1.11 - [\text{glucose}]_{72}}{1.11 - ([\text{glucose}]_{72} - [\text{glucose}]_8)} \times 100\ \%$$

$$\text{Gluonic acid selectivity from converted glucose} = \frac{[\text{gluconic } acid]_8}{1.11 - [\text{glucose}]_{72}} \times \frac{45}{49} \times 100\ \%$$

$[glucose]_8$ and $[glucose]_{72}$ are corresponding to the mass concentration of glucose solution after 8-h photobiocatalytic reaction and subsequent 72-h hydrolytic reaction, respectively. $[gluconic\ acid]_8$ represents the mass concentration of gluconic acid after 8-h photobiocatalytic reaction.

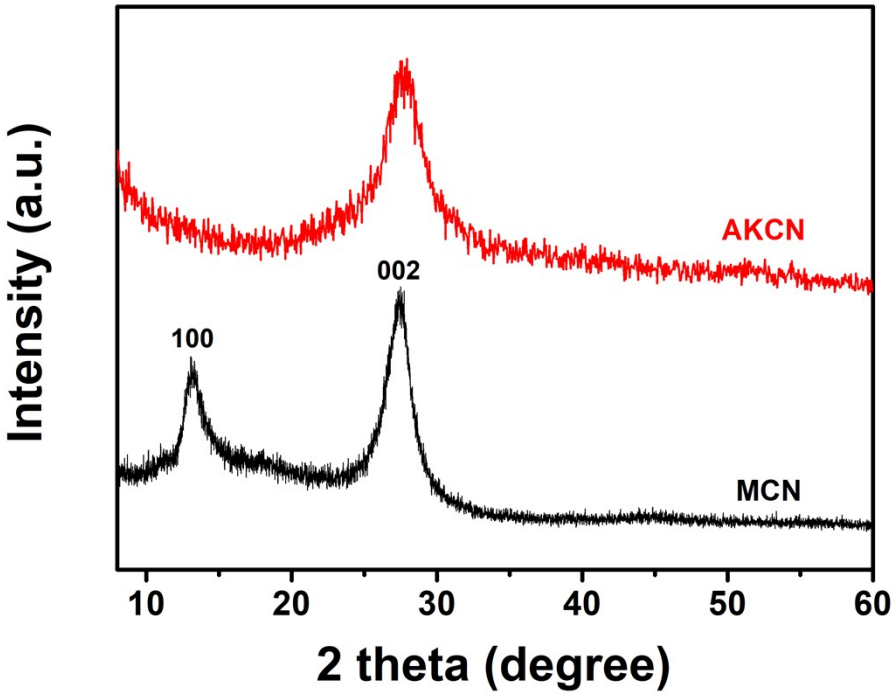

Fig. S1. XRD patterns of MCN and AKCN.

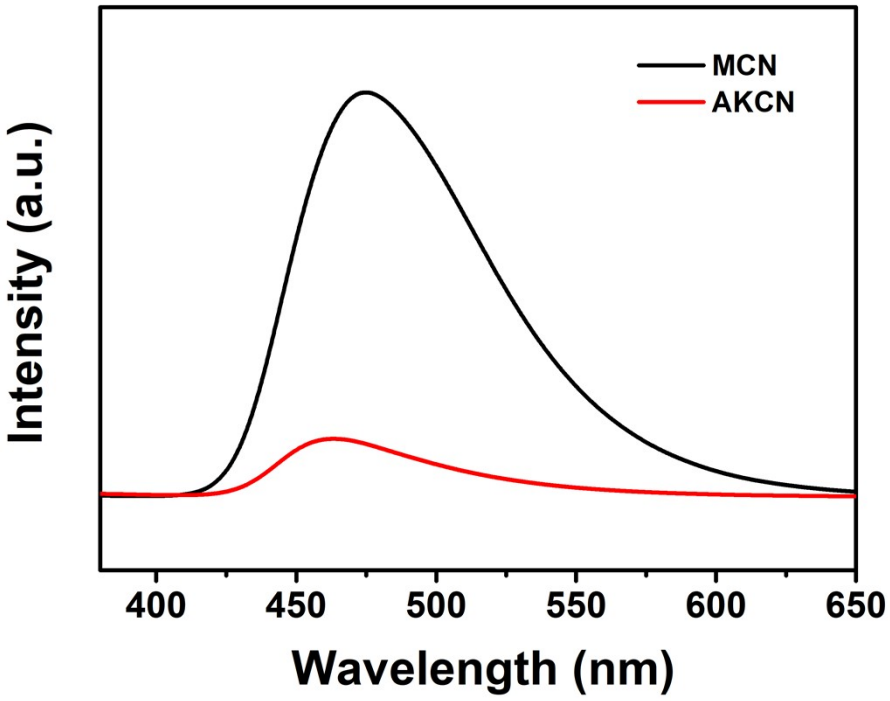

Fig. S2. PL spectra of MCN and AKCN.

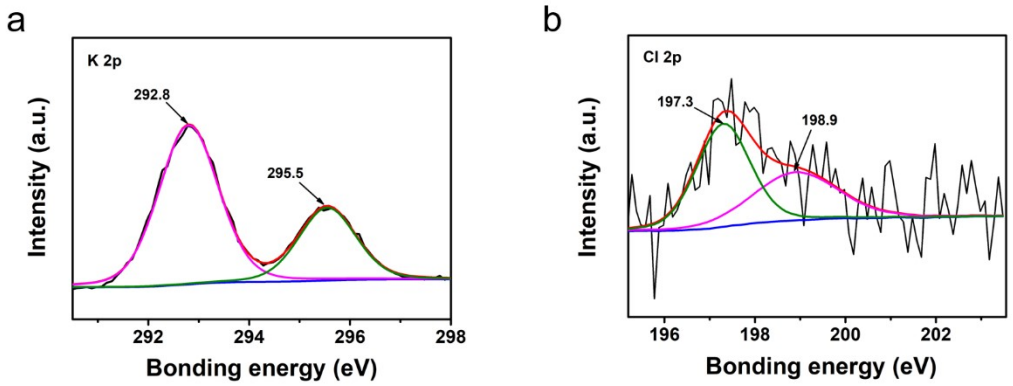

Fig. S3. High-resolution XPS spectra of (a) K 2p and (b) Cl 2p of AKCN.

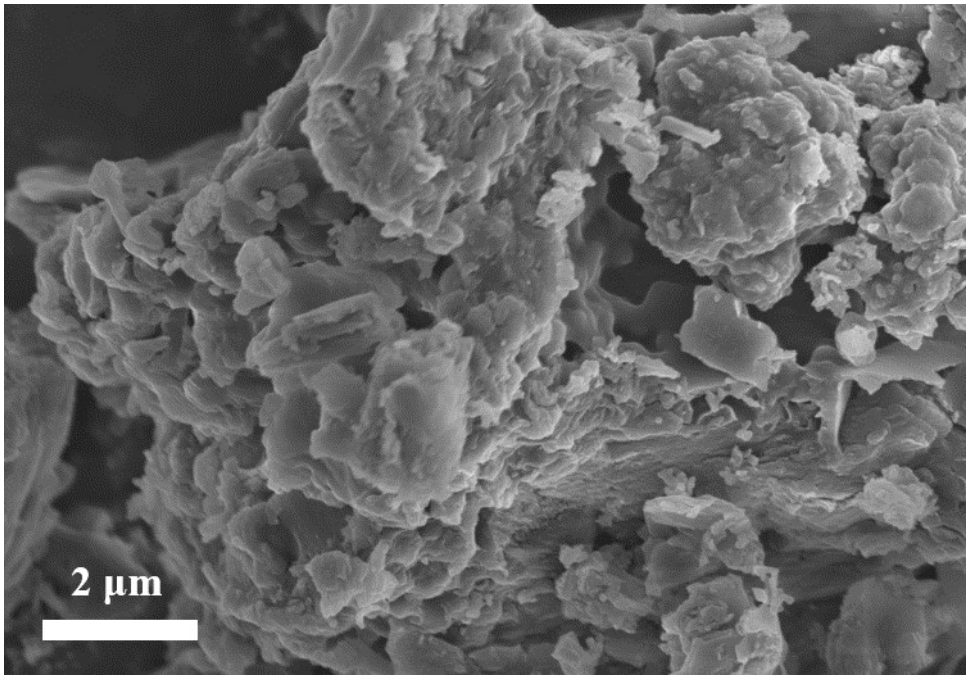

Fig. S4. FESEM image of MCN.

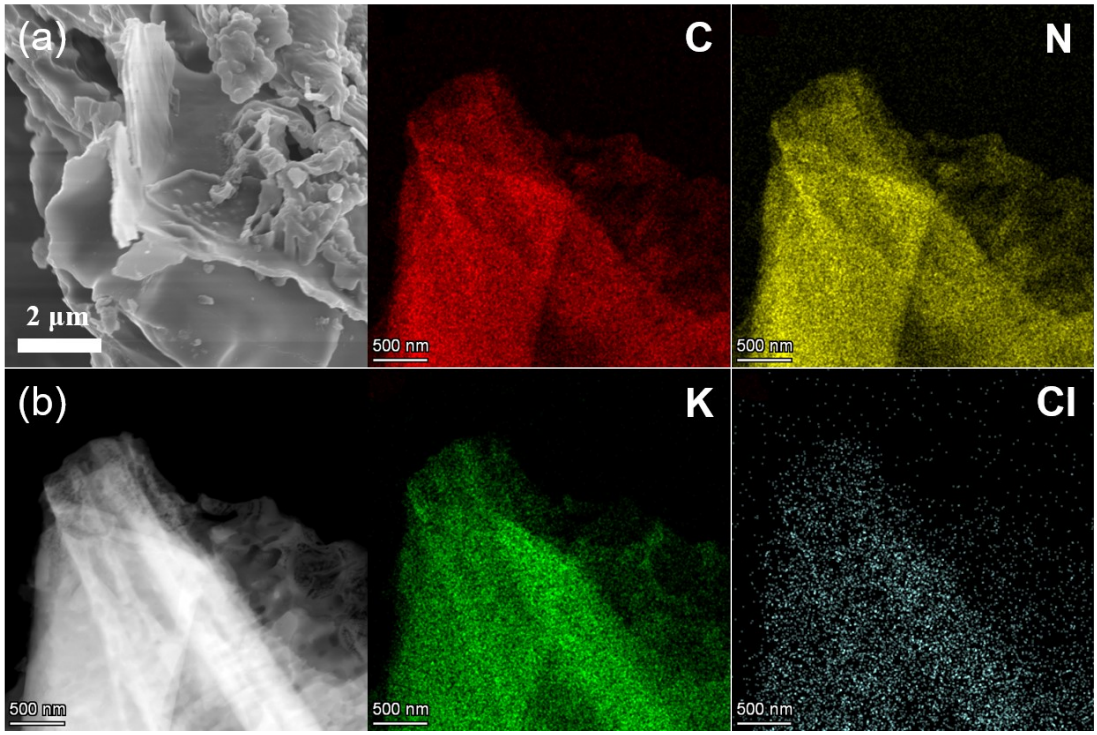

Fig. S5. (a) FESEM image and (b) HAADF-STEM image of AKCN and corresponding elemental mappings of C, N, K, Cl.

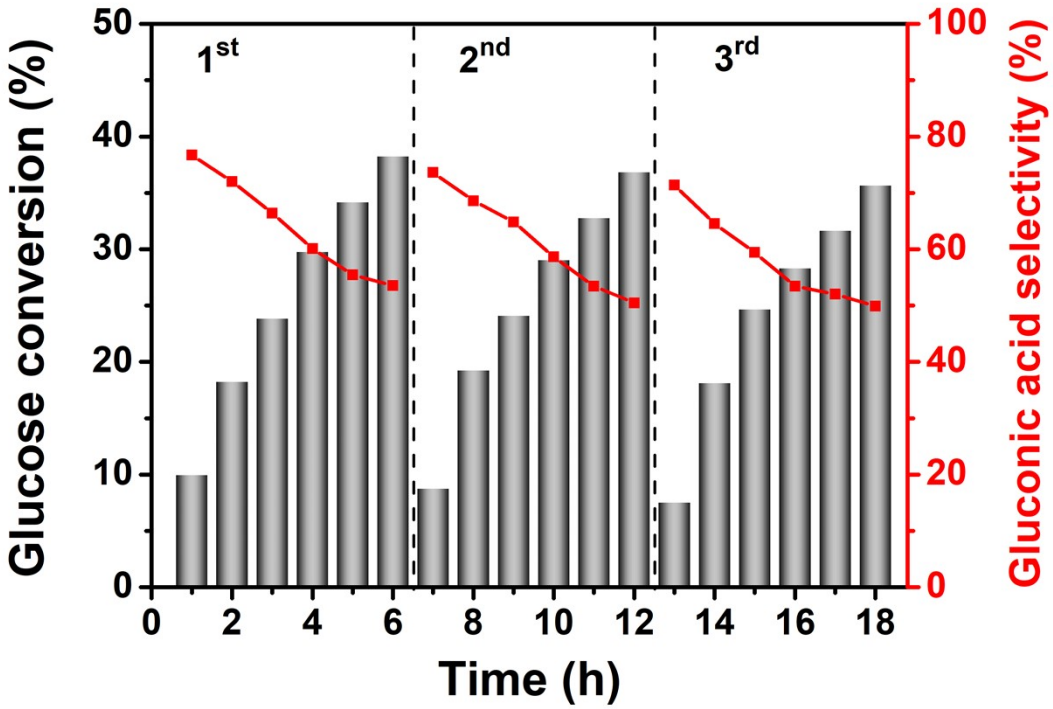

Fig. S6. The recyclability of AKCN for glucose photo-oxidation into gluconic acid during three cycles.

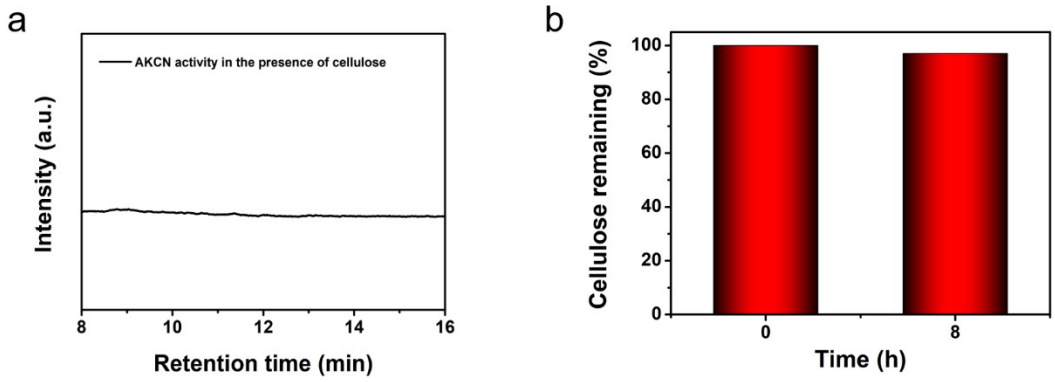

Fig. S7. (a) HPLC measurements of AKCN in the presence of cellulose and (b) cellulose remaining after 8-h photocatalytic reaction.

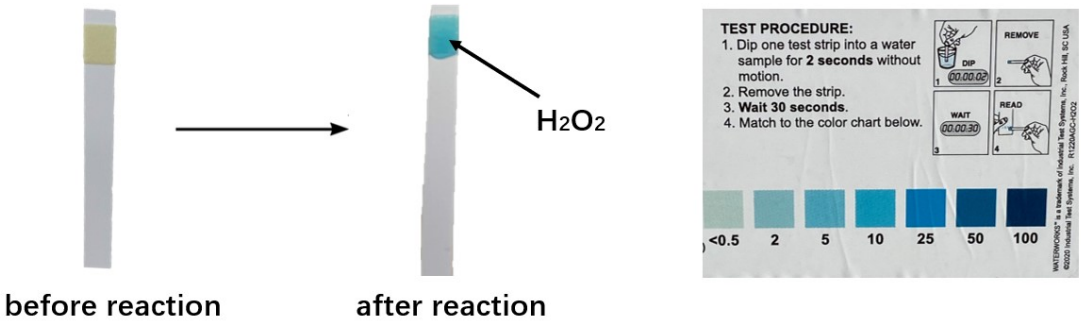

Fig. S8. Photograph of the H_2O_2 test strip measuring the solution before and after reaction.

After 8-h photobiocatalytic reaction, one H_2O_2 test strip was dipped into the reaction solution for two seconds without motion. It was found that the color of H_2O_2 test strip changed from yellow to blue, indicating the formation of H_2O_2 in the photobiocatalytic reaction.

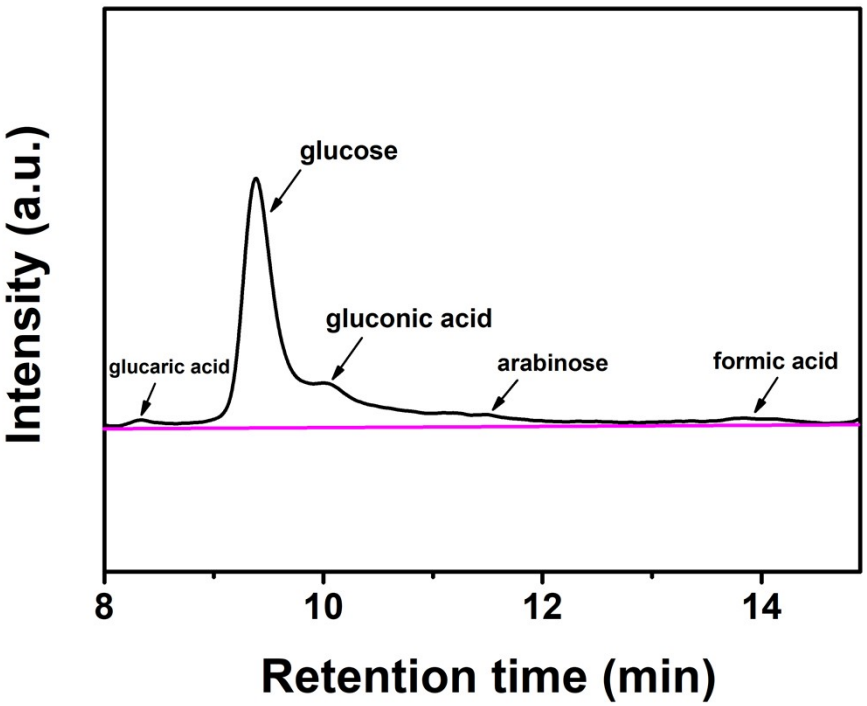

Fig. S9. HPLC measurements of aqueous solution from AKCN sample upon 8-h illumination.

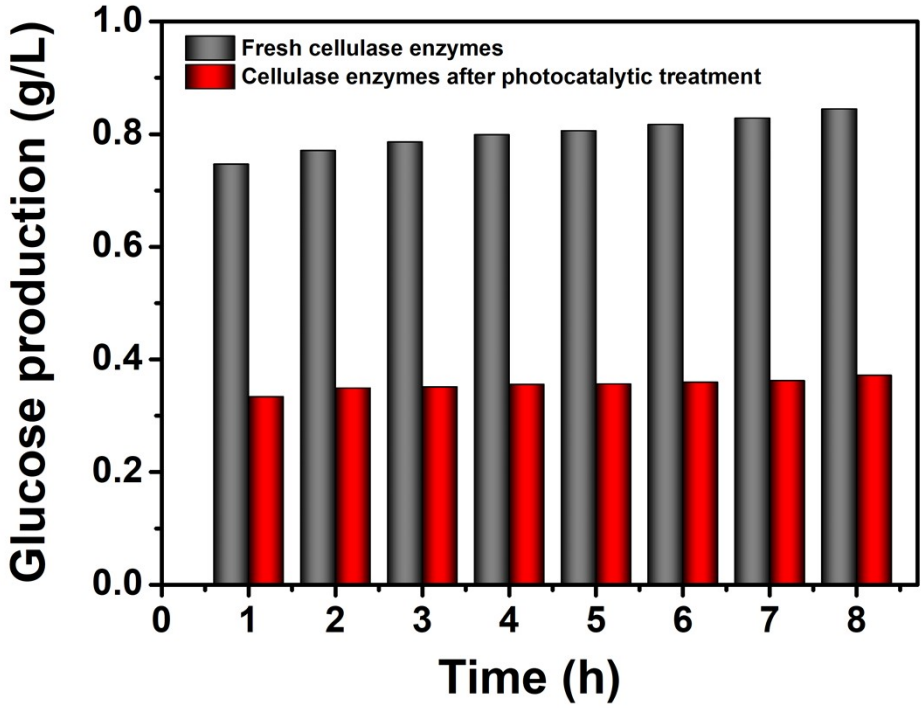

Fig. S10. Glucose production during 8-h enzymatic hydrolysis of fresh cellulase enzymes and cellulase enzymes after 8-h photocatalytic treatment. Note: The 8-h photocatalytic treatment with cellulase enzymes and photocatalyst was carried out under same conditions, followed by the addition of cellulose (1g/L) into the system to study the cellulase enzymes activity during 8-h enzymatic hydrolysis.

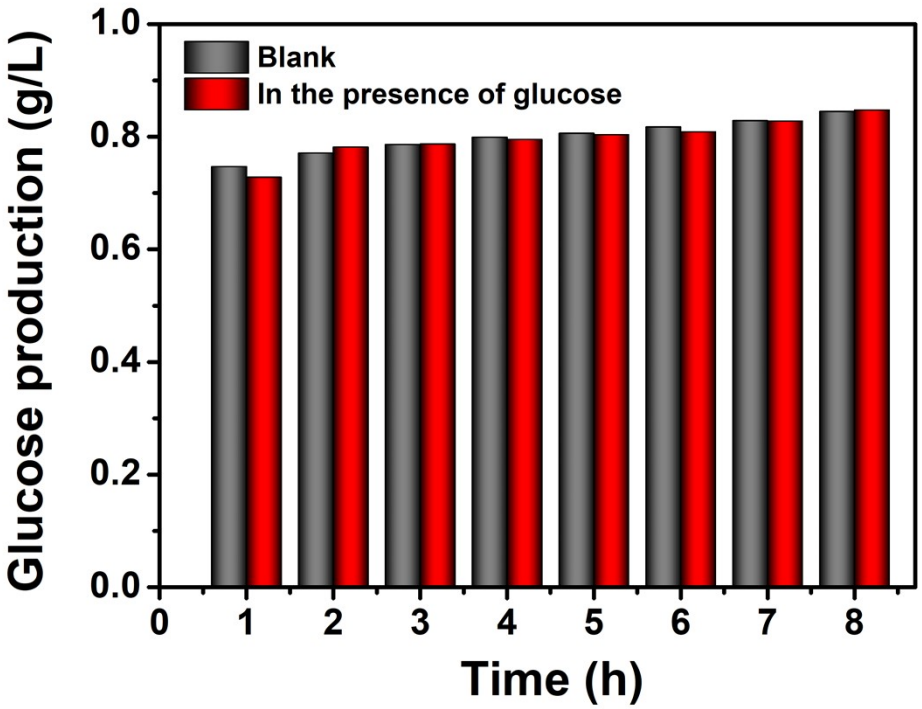

Fig. S11. Glucose production from cellulose hydrolysis (1 g/L) of the enzymes in the absence or presence of glucose (0.1 g/L) under 8-h enzymatic hydrolysis.

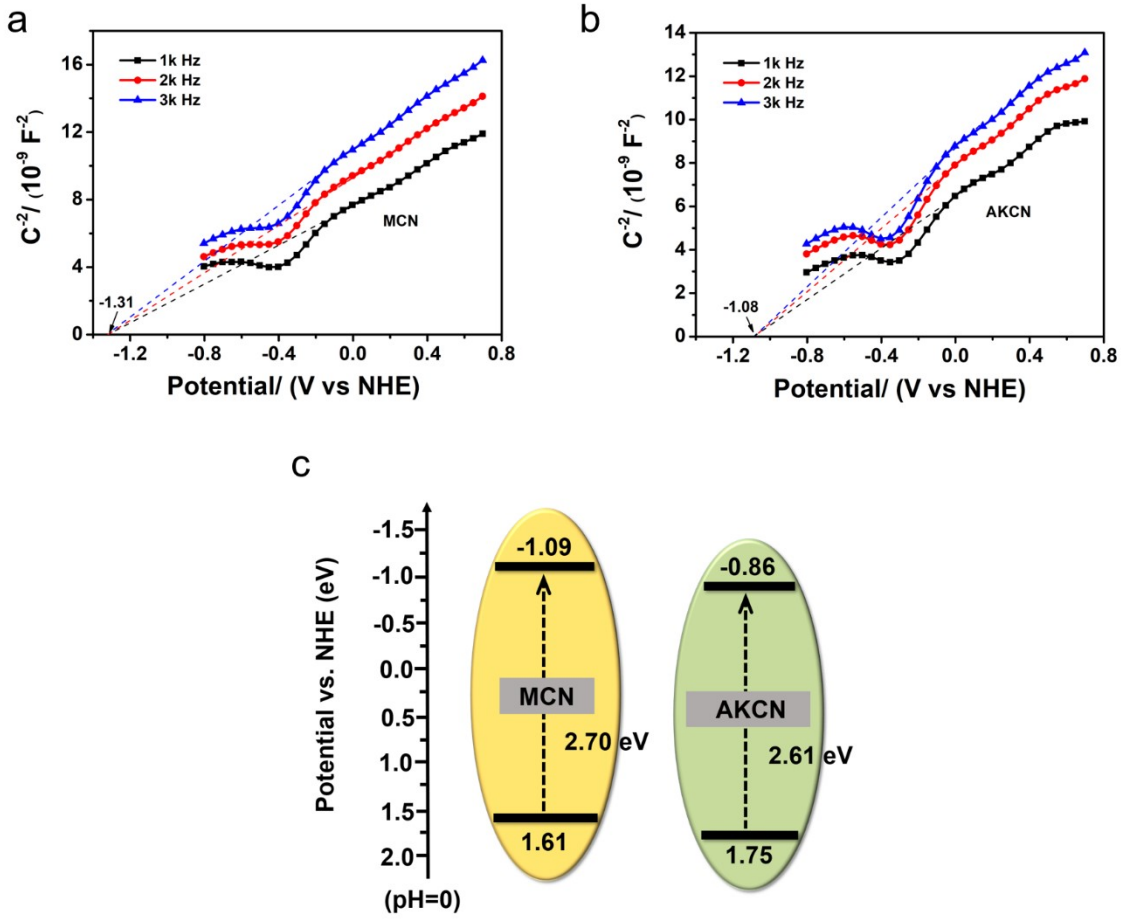

Fig. S12. Mott-Schottky plots collected at different frequencies of (a) MCN and (b) AKCN. (c) Band structure of MCN and AKCN.

Table S1. The summary of cellulose or derived carbohydrates catalytic conversion into value-added products.

Substrate	Catalyst	Time	Tempera-ture	Main products (Yield %)	Ref.
Cellulose	$H_5PV_2Mo_{10}O_{40}$ & HCl	9 h	170 °C	Formic acid (34%)	4
Cellulose	ZrO_2-Al_2O_3	6 h	200 °C	Lactic acid (25%)	5
Cellulose	Fe_3O_4–SBA–SO_3H	3 h	150 °C	Levulinic acid (42%)	6
Cellulose	$Au/Cs_{2.6}H_{0.4}PW_{12}O_{40}$	11 h	145 °C	Gluconic acid (47%)	7
Cellobiose	CuO-CeO_2	3 h	160 °C	Gluconic acid (51%)	8
Cellobiose	0.5Co–0.5Au/TiO_2	3 h	145 °C	Gluconic acid (33%)	9
Glucose	Pt/C	1 h	200 °C	Gluconic acid (22%)	10
Glucose	ZnO/$CoPzS_8$(0.5%)	5 h	25 °C	Gluconic acid (7%)	11
Glucose	TiO_2/HPW(29%)/CoPz(1%)	3 h	25 °C	Gluconic acid (14%)	12
Glucose	TiO_2	0.2 h	30 °C	Gluconic acid (8%)	13
Glucose	SnO_2/$FePz(SBu)_8$	3 h	25 °C	Gluconic acid (11%)	14
Cellulose	AKCN	8 h	50 °C	Gluconic acid (24%)	This work

Table S2. The fluorescence lifetimes and relative percentage of MCN and AKCN.

Sample	τ_{av}(ns)	τ_1(ns) (rel. %)	τ_2(ns) (rel. %)	τ_3(ns) (rel. %)
MCN	18.42	2.03(33.6)	9.61(43.8)	59.85(22.6)
AKCN	3.65	0.68(48.9)	3.22(43.4)	24.91(7.7)

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