Supplementary Information:

**Experimental details and methods**

## 1. Biomass degradation with POM at elevated temperature

Phosphomolybdic acid ($H_3[PMo_{12}O_{40}]$, noted as $PMo_{12}$) was purchased from TCI America. Several biomasses were used in the degradation experiments at an elevated temperature, including potato starch, cellulose, lignin, glucose, switchgrass, poplar powder and fresh algae. Potato starch was provided by Gain Processing Corporation. Crystalline cellulose was purchased from Alfa Aesar. The cellulose suspension was homogenized for 40 min to form a small particle suspension in the solution before used. Lignin was isolated from a commercial USA softwood Kraft pulping liquor. Switchgrass was from Ceres, Inc. (Thousand Oaks, CA, USA) and poplar was provided by Michigan State University. Switchgrass and poplar samples were washed with DI water then dried at 45 °C overnight. The dry samples were then milled in a Wiley mill through a 0.8 mm screen, yielding the biomass powder directly used in this study without any chemical pretreatment. Algae (*Scenedesmus quadricauda*) was provided by Yongsheng Chen's group at Georgia Institute of Technology. The collected algae suspension was directly used without any pre-treatment.

Biomass degradation experiments were conducted in aqueous solution by simple heating. Take glucose for example, calculated amount of glucose (Alfa Aesar) was added to yellow $PMo_{12}$ solution with magnetic stirring until dissolved. The concentrations of $PMo_{12}$ and glucose were 0.3 mol $l^{-1}$ and 2 mol $l^{-1}$ respectively (noted as glucose-$PMo_{12}$ solution). 10 ml of the glucose-$PMo_{12}$ solution was transferred to the glass vessel and continuously refluxed at 100 °C in the dark for 90 min. The color of the solution turned from yellow to deep blue. After it cooled to room temperature, calculated DI water was added to maintain the total volume of 10 ml. Very small amount of solution was taken out as a sample then diluted to 1 mmol $l^{-1}$ $PMo_{12}$ solution for analysis of the concentration of reduced $PMo_{12}$ by spectrophotometry (method see part 5).

Degradation of other biomass has the same procedure as degradation of glucose. The concentrations of $PMo_{12}$ and biomass powder were 0.3 mol $l^{-1}$ and 15 g $l^{-1}$ respectively. The biomass-$PMo_{12}$ mixture was continuously refluxed at 100 °C for 4 hours. It should be noted that some raw biomasses were in the form of particle suspended initially then gradually dissolved in the POM aqueous solution during the degradation with $PMo_{12}$. Finally, homogenous deep blue biomass-solutions were obtained.

The kinetics of reduction reaction of $PMo_{12}$ was investigated in the degradation of glucose, starch and lignin. During the heating with $PMo_{12}$, very small amount of solution was taken out as a sample at regular intervals. The samples were diluted to 1 mmol $l^{-1}$ $PMo_{12}$ solution for analysis of the concentration of reduced $PMo_{12}$.

## 2. Biomass degradation with POM under light irradiation

In the photo-degradation experiments, ethylene glycol, glycerol and glucose were used. These alcohols were purchased form Alfa Aesar. The concentrations of $PMo_{12}$ and alcohols were 0.3 mol $l^{-1}$ and 2 mol $l^{-1}$ respectively. The mixed alcohols-$PMo_{12}$ solution (10 ml) was stored in the glass vessel and irradiated with AM 1.5-type simulated sunlight (SoLux Solar Simulator, New York, US) for 8 hour with a distance of 10 cm from the reactor surface. The color of the solution gradually turned from yellow to blue. After

the irradiation, very small amount of solution was taken out as a sample then diluted to 1 mmol $l^{-1}$ $PMo_{12}$ for analysis of the concentration of reduced $PMo_{12}$ by spectrophotometry.

Silicotungstic acid ($H_4SiW_{12}O_{40}$ noted as $SiW_{12}$, purchased from Alfa Aesar) was also used in the photo-degradation. The concentrations of $SiW_{12}$ and alcohols were 0.3 mol $l^{-1}$ and 2 mol $l^{-1}$ respectively. The mixed alcohols-$SiW_{12}$ solution (10 ml) was stored in an airtight quartz vessel (shown in Fig. S3 C). In order to prevent the re-oxidation of reduced $SiW_{12}$, air in the quartz vessel was purged by pure $N_2$ gas before the light irradiation. The degradation was conducted at room temperature with irradiated with UV light (OmniCure S2000, Lumen Dynamics Group Inc., Canada) for 1 hour with a distance of 10 cm from the reactor surface. The UV irradiation intensity was determined by a radiometer (ILT 1400-A, International Light Technologies, Inc., US), showing the irradiation intensity was 60 mW $cm^{-2}$. The irradiation area in UV degradation was 15.8 $cm^2$. In order to analyze the concentration of reduced $SiW_{12}$, very small amount of solution was taken out as a sample then diluted to 50 mmol $l^{-1}$ $SiW_{12}$ using oxygen removed DI water.

The photo-degradation was also conducted under actual sunlight irradiation. The solutions contained 0.3 mol $l^{-1}$ $SiW_{12}$ and 2 mol $l^{-1}$ alcohols were stored in quartz vessel and protected with pure $N_2$ gas, at the same time, were irradiation under the sunlight for 6 hours (9:00 AM-3:00 PM, March 24th, Atlanta, atmospheric temperature 16 °C). The irradiation area in sunlight degradation was 15.8 $cm^2$ and average sunlight irradiation intensity was 6.16 mW $cm^{-2}$. After the degradation, the deep blue solutions were store in glass vessel under $N_2$ protection.

**3. Assembly of electrolysis cell and test methods.**

The bipolar plates of the electrolysis cell were made of high-density graphite plates with a serpentine flow channel 2 mm wide, 10 mm deep, and 5 cm long (total geometry projected area of 1 $cm^2$). The graphite felt was purchased from Alfa Aesar, and was pretreated with concentrated sulphuric and nitric acids in a 3:1 volumetric ratio at 50 °C for 30 min. Then the graphite felt was washed with DI water until the pH of the wash became neutral, dried at 80 °C and cut to pieces with 2 mm width and 10 mm thick. These graphite electrodes were filled into the channel of anode plant.

Nafion® 115 (127 micrometers thick, purchased from DuPon™) was used as proton exchange membrane in this direct biomass fuel cell. The membrane was pretreated in the boiling solution of 1 mol $l^{-1}$ $H_2SO_4$ (Aldrich) and 3% $H_2O_2$ (Aldrich) for 30 min, then was washed and soaked in DI water.

The Nafion membrane was sandwiched between two graphite flow-field plates. The graphite-felts were filled into the channel of anode plant. A 5-layer gas diffusion electrode (FuelcellsEtc, US) was used as cathode electrode. The anode and cathode graphite flow-field plates were clamped between two acrylic plastic end plates. PTFE gaskets were included on the circumference of the graphite flow-field plates to prevent any leakage. PTFE tubing was used to connect the fuel cell and a pump that can transport electrolyte solutions into and out of the electrode cell.

In the electrolysis experiments, obtained biomass-$PMo_{12}$ or $SiW_{12}$ solution was stored in anode tank and $H_3PO_4$ solution (1 mol $l^{-1}$) was stored in cathode tank then pumped through the anode and cathode cell respectively. The temperature of the liquid in the cell was 80 $^oC$. Practically, the anode and cathode solutions were 10 ml with a flow rate of 30 ml $min^{-1}$.

In order to measure the produced hydrogen gas, the outlets of cathode cell passed through a cooling column (0°C) in order to separate water vapor and hydrogen. The rate of hydrogen production was followed by gas-volume measurements. Gas products from both anode and cathode were collected and analyzed by gas chromatograph (Varian 490 micro-GC).

A Versa Stat 3 electrochemical working station (Princeton Applied Research) was used to examine the I-V curves using the controlled potentiostatic method.

Glucose was used as feed stock in the continuous running. $PMo_{12}$ or $SiW_{12}$ (0.3 mol $l^{-1}$) solution mixed with glucose (2 mol $l^{-1}$) was stored in the anode tank. Redox reaction was conducted by heating or UV light irradiation. At the same time, the glucose-$PMo_{12}$ or $SiW_{12}$ solution was pumped through the anode cell, and the $H_3PO_4$ solution (1 mol $l^{-1}$) was pumped through the cathode cell. After heating or irradiation for 1 hour, the color of glucose-$PMo_{12}$ or $SiW_{12}$ solution turned to deep blue, then the required electric field was applied. The continuous running was controlled by Versa Stat 3 electrochemical working station using constant current discharging at the current density of 50, 100 and 200 mA $cm^{-2}$ respectively. The hydrogen production rate was measure by gas flow meter and was also cross-checked via Faraday's law calculations.

**4. Analysis of reduction degree of POM**

The reduction degree of $PMo_{12}$ was determined by spectrophotometry. In order to obtain the calibration curve, 20 ml $PMo_{12}$ solution (0.1 mol $l^{-1}$) without organics was reduced by electrochemical reduction treatment at 3V for different times. 1 ml of the reduced $PMo_{12}$ solution was taken out as a sample then diluted to 1 mmol $l^{-1}$ for absorbance determination at 700 nm. 15 ml of the reduced $PMo_{12}$ solution was taken out then titrated with potassium permanganate solution (calibrated by standard sodium oxalate first). Therefore, the calibration curve of 1 mmol $l^{-1}$ $PMo_{12}$ at different reduction degrees was obtained.

The concentration of $Mo^{5+}$ in the biomass-$PMo_{12}$ reaction solution was measured by the UV-Visible spectrophotometer. Samples were diluted to 1 mmol $l^{-1}$of total $PMo_{12}$ concentration and then were used for UV-Vis measurement at 700 nm. Reduction degree was used in the calculation of numbers of electrons that transferred from starch to $PMo_{12}$ during light irradiation or heating process.

The determination of reduction degree of $SiW_{12}$ has the same procedure as the determination of $PMo_{12}$. It should be noted that $SiW_{12}$ can re-oxidized by oxygen in air. Therefore, DI water requires deoxygenation by $N_2$ purging.

**5. Other characterizations**

**SEM.** The Zeiss LEO 1530 microscopy was used for SEM imaging of graphite felt electrode.

**NMR.** All NMR spectral data reported in this study were recorded with a Bruker Avance/DMX 400 MHz NMR spectrometer. Quantitative $^{13}C$ NMR employed an inverse gated decoupling pulse sequence, 90° pulse angle, a pulse delay of 5 s and 6,000 scans. Quantitative $^{1}H$ NMR was acquired with 16 scans and 1 s pulse delay. The biomass-$PMo_{12}$ sample was treated with repeated heating and electrolysis process, then was dried at 80 °C in vacuum and re-dissolved in $D_2O$ for the $^{13}C$ and $^{1}H$ NMR.

**HPLC-MS.** The final glucose-$PMo_{12}$ solutions after several thermal degradation and electrolysis circles were collected and neutralized with CsCl (Aldrich). Thus, $PMo_{12}$ can be precipitated and separated by

centrifugation. The obtained supernatant was diluted to 10 mg $ml^{-1}$ with DI water for liquid chromatography-mass spectrometry (LC-MS) measurement.

A 5957C Agilent MS detector was used in EI (70 keV) mode to identify the biomass species that were produced in the reaction system. For LC-MS analysis, an Agilent 1100 HPLC system equipped with a ZIC-HILIC column (2.1×100 mm) was used to separate the components. Mixture of acetonitrile (25 ml) and water (200 ml) was used as mobile phase with the flow rate 100 μL $min^{-1}$. The Micromass Quattro LC was equipped for the MS analysis.

**GPC.** Gel permeation chromatography (GPC) was utilized to determine the changes in molecular weight during the thermal degradation of polymeric biomass with $PMo_{12}$. Samples were taken from the reaction solution at different times, and neutralized with CsCl (Aldrich) to separate $PMo_{12}$. The final concentration of organic substance was around 1 mg $ml^{-1}$ with pH 10. The analysis was performed on an Agilent 1200 HPLC system (Agilent Technologies Inc, Santa Clara, CA, US) equipped with Ultrahydrogel columns (Waters Corporation, Milford, MA, US) and an Agilent RI detector using DI water as the mobile phase (0.5 ml $min^{-1}$) with injection volumes of 25μL.

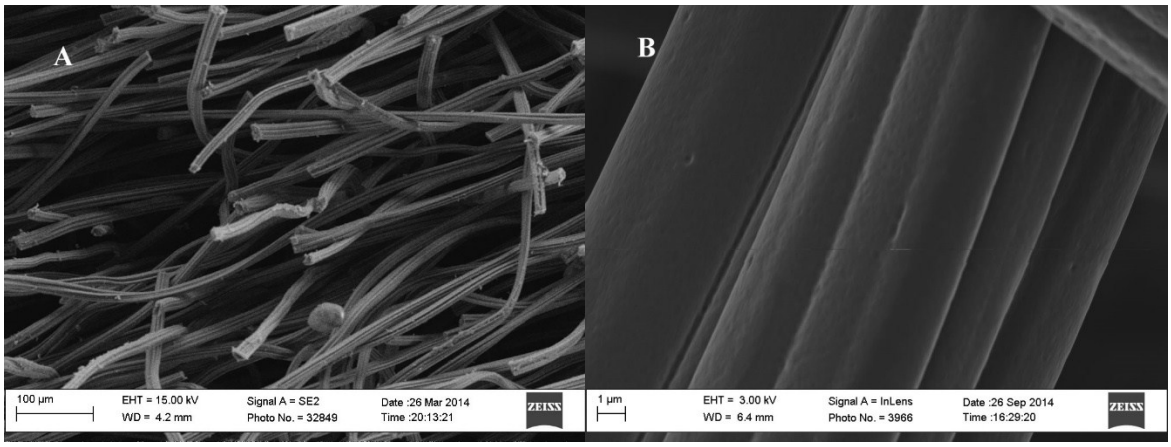
**Cyclic voltammogram.** The measurements were taken on Versa Stat 3 electrochemical working station using a saturated calomel reference electrode, a Pt wire counter electrode and a 3 mm diameter graphite electrode. Electrode potentials were converted to the Normal hydrogen electrode (NHE) scale using the equation E(NHE)=E(SCE)+0.2415 V, where E(NHE) is the potential versus Normal hydrogen electrode and E(SCE) is the measured potential versus saturated calomel reference electrode.

**Electrode Potential.** The electrode potentials (E) of the initial and reduced $PMo_{12}$ and $SiW_{12}$ solutions were measured using a saturated calomel reference electrode, a 3 mm diameter graphite electrode and a standard multimeter (DMM 4050 6-1/2 Digit Precision Multimeter, Tektronix) for independent voltage measurements. The E values were given in volts relative to the Normal Hydrogen Electrode (NHE).

**GC.** In order to collect and analyze the emission gas during the reaction of glucose-$PMo_{12}$ solution, a gas collection bag was connected to the anode tank that stored with glucose-$PMo_{12}$ solution. After repeated heating and electrolysis cycles, the composition of gas was analyzed on Varian 490 micro-GC equipped with a Pora Plot U column.

**TOC.** TOC analysis was taken on carbon analyzer (model 1555B, Ionics, Incorporated).

**Supporting Figures**



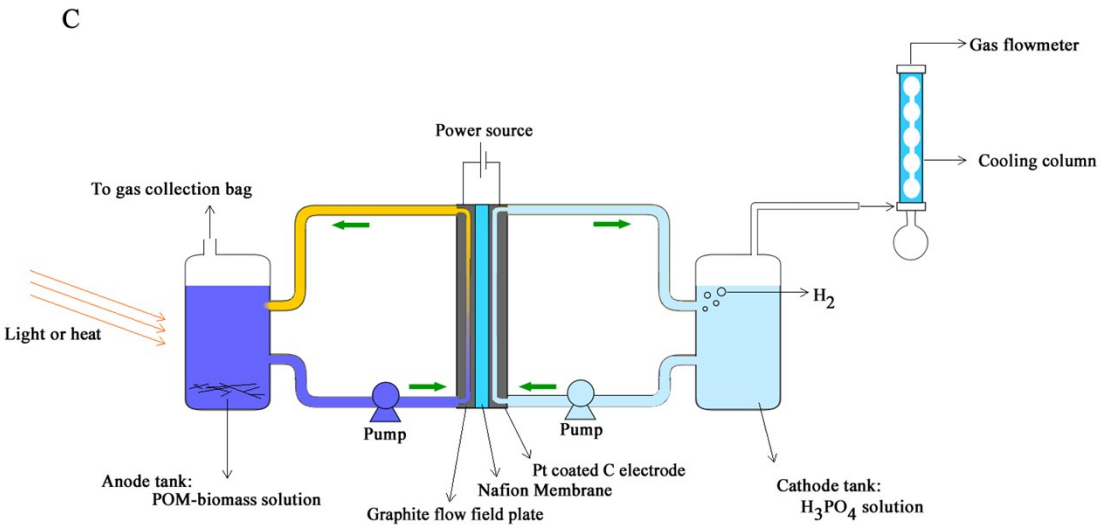




Figure S1 (A) SEM image of graphite-felt electrode; (B) a magnified view of graphite fibers; (C) experimental set-up for the study of direct biomass electrolysis in a proton exchange membrane electrolysis cell (PEMEC).

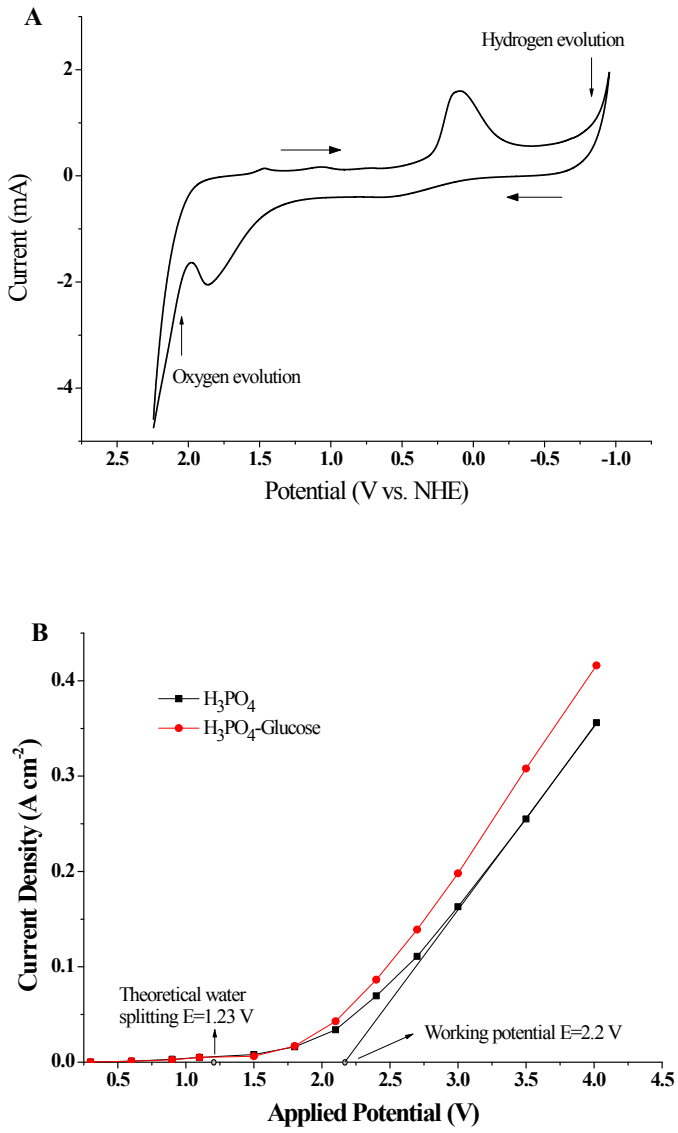



Figure S2 (A) cyclic voltammetry of $H_3PO_4$ solution (1 mol $l^{-1}$) on graphite electrode (0.157 $cm^2$) with scan rate 10 mV $s^{-1}$ at room temperature; (B) Polarization curves of pure $H_3PO_4$ solution (1 mol $l^{-1}$) and $H_3PO_4$-glucose solution (1 mol $l^{-1}$, 2 mol $l^{-1}$ respectively) in an extended applied potential range.

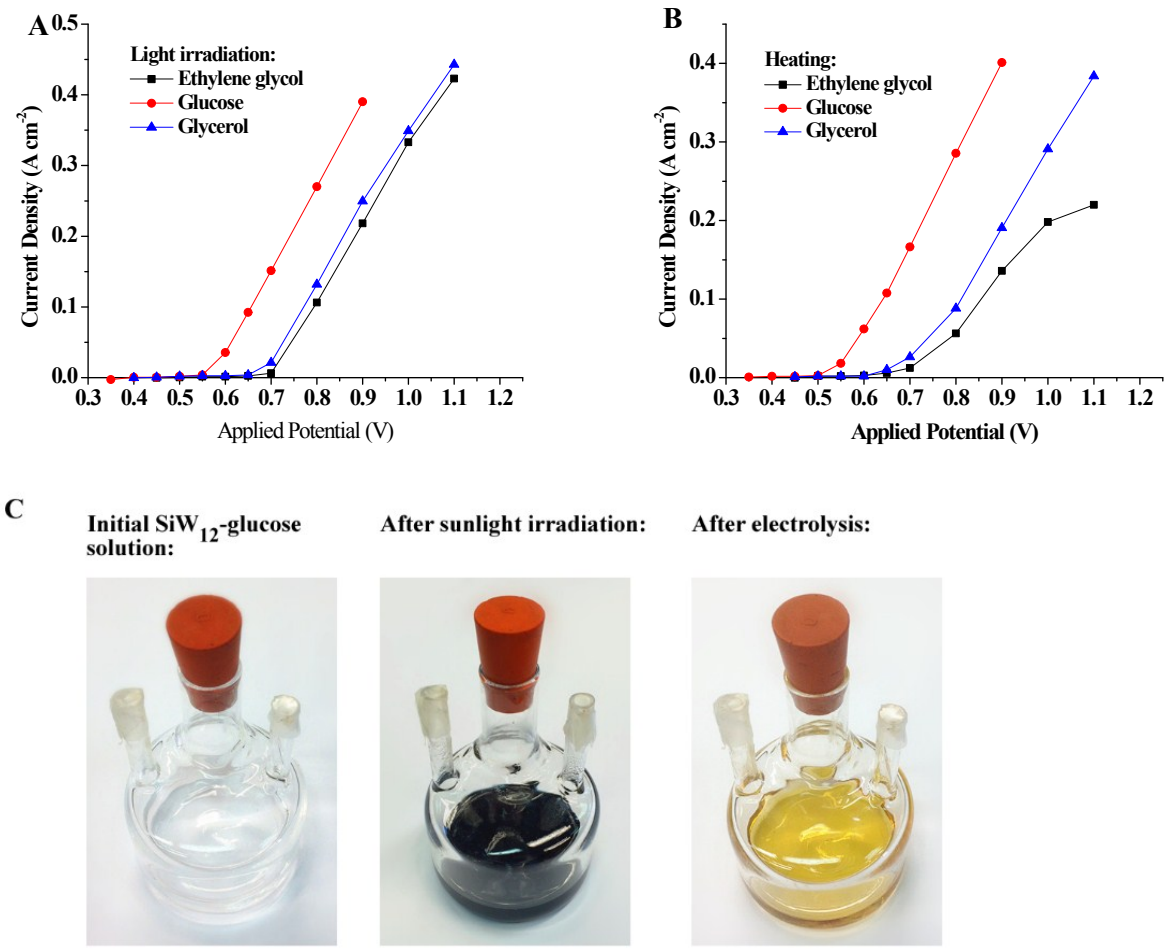



Figure S3 (A) Polarization curves of $PMo_{12}$ (0.3 mol $l^{-1}$) and bio-derived alcohols (2 mol $l^{-1}$) solutions pre-irradiated with AM 1.5-type simulated sunlight for 8 hour with a distance of 10 cm from the reactor surface. The volume of solution was 10 ml and irradiation area was 15.8 $cm^{-2}$. (B) Polarization curves of $PMo_{12}$ (0.3 mol $l^{-1}$) and bio-derived alcohols (2 mol $l^{-1}$) solutions preheated at 100 °C for 2 hours. (C) The $SiW_{12}$-glucose solution that used in the sunlight irradiation-electrolysis cycle. In order to prevent the re-oxidation of reduced $SiW_{12}$ during the light irradiation, air in the quartz vessel was purged out by pure $N_2$ gas before irradiation.

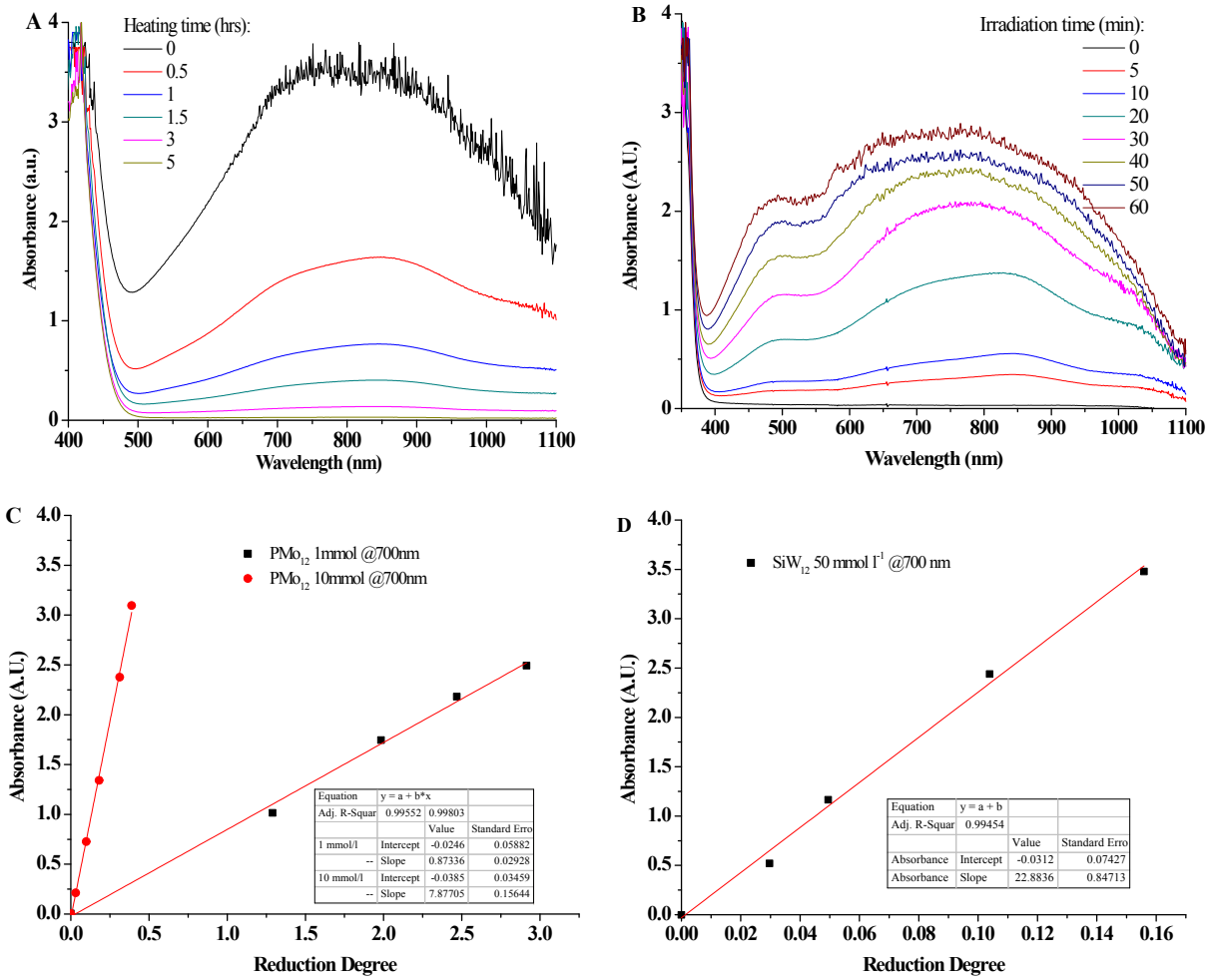



Figure S4 (A) UV-Vis spectrum of starch-$PMo_{12}$ solution during the thermal degradation process (diluted to 1mmol $l^{-1}$); (B) UV-Vis spectrum of glucose-$SiW_{12}$ solution during the UV irradiation process (diluted to 50 mmol $l^{-1}$); (C) calibration curve for $PMo_{12}$ solution with different reduction degrees; (D) calibration curve for $SiW_{12}$ solution with different reduction degrees.

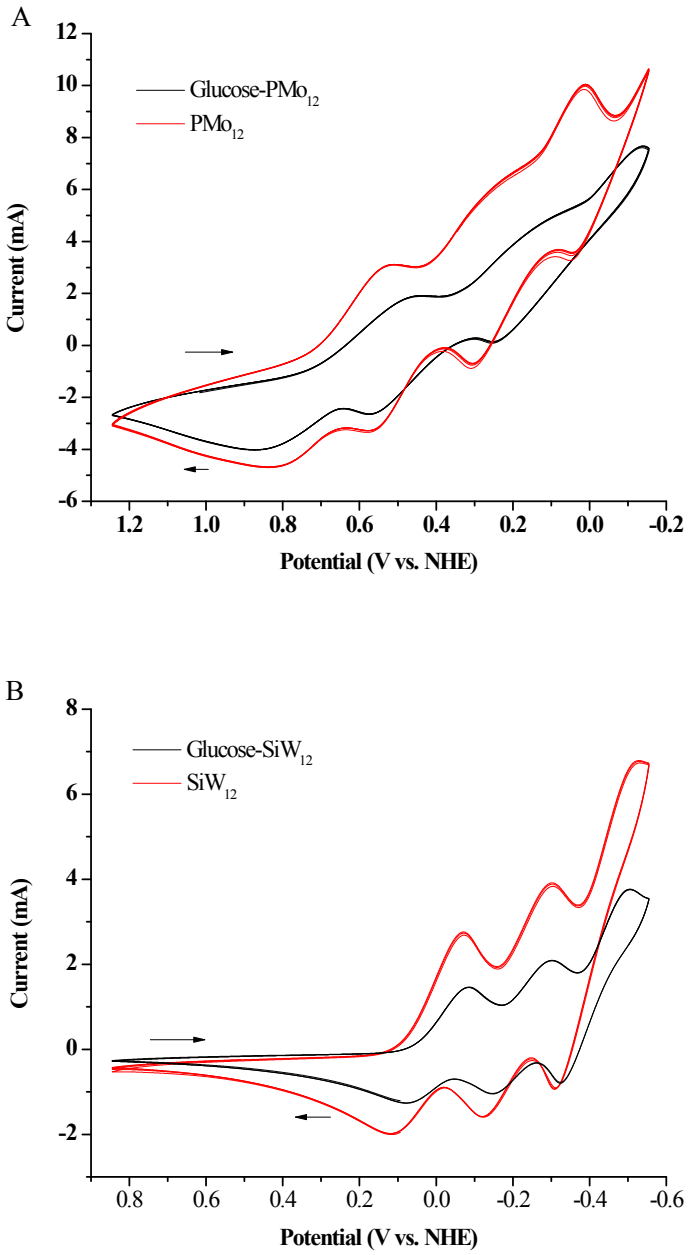



Figure S5 (A) cyclic voltammetry of pure $PMo_{12}$ solution (1 mmol $l^{-1}$) and glucose-$PMo_{12}$ solution (2 mol $l^{-1}$ and 1 mmol $l^{-1}$ respectively) on graphite electrode (0.157 $cm^2$) with scan rate 10 mV $s^{-1}$; (B) cyclic voltammetry of pure $SiW_{12}$ solution (1 mmol $l^{-1}$) and glucose-$SiW_{12}$ solution (2 mol $l^{-1}$ and 1 mmol $l^{-1}$ respectively) on graphite electrode with scan rate 10 mV $s^{-1}$. POM solution and glucose-POM solution have similar electric performance on graphite electrode. No redox peaks obtained in the cyclic voltammetry of glucose-POM solution, which demonstrates that glucose was not directly oxidized on graphite electrode under the conditions in our experiments.

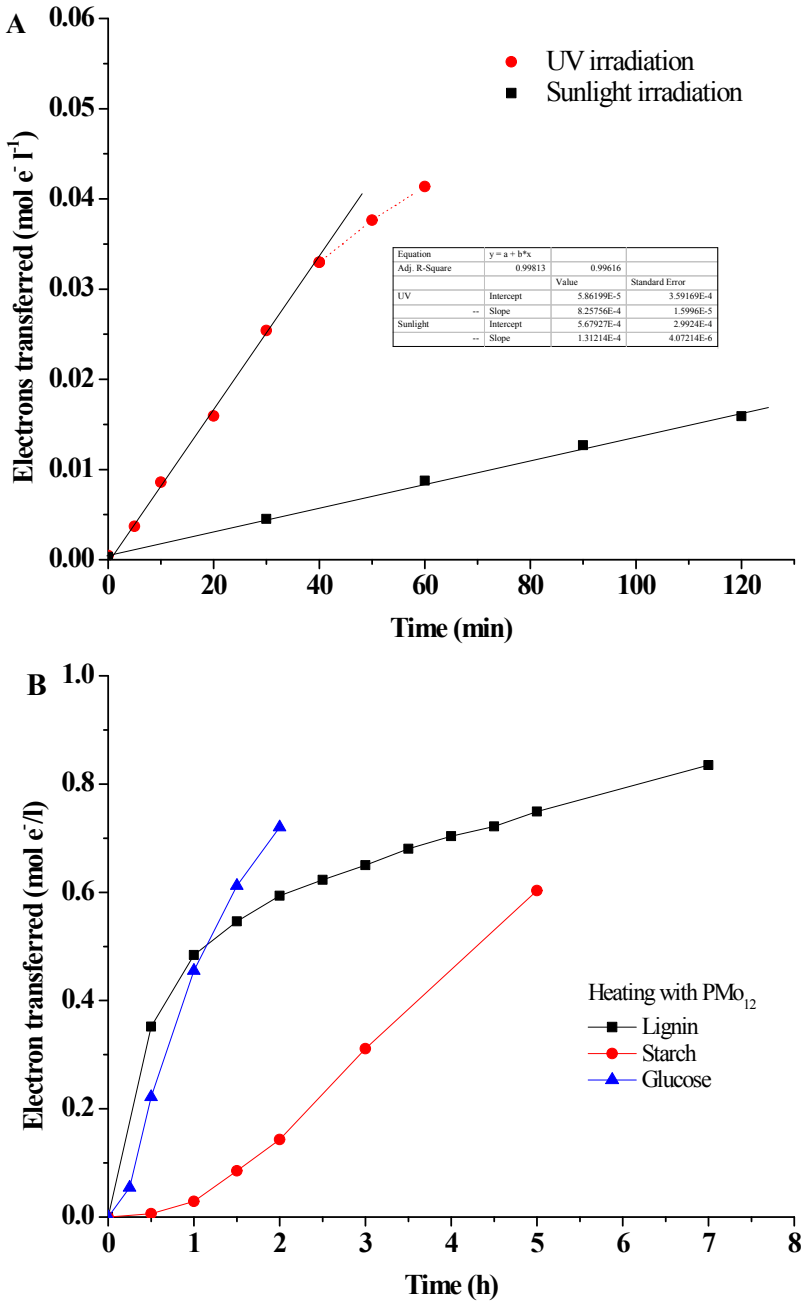



Figure S6 (A) Reaction rates between glucose (2 mol $l^{-1}$) and $SiW_{12}$ (0.3 mol $l^{-1}$) under the UV (irradiation density 60 mW $cm^{-2}$; irradiation area 15.8 $cm^2$; solution volume 10 ml) and actual sunlight irradiation (9:00 AM-3:00 PM, March 24th, Atlanta, atmospheric temperature 16 °C; irradiation density 6.16 mW $cm^{-2}$; irradiation area 15.8 $cm^2$; solution volume 10 ml); (B) Reaction rates between different biomass and $SiW_{12}$ (0.3 mol $l^{-1}$) with simple heating. The concentration of lignin, starch is 15 g $l^{-1}$ and concentration of glucose is 2 mol $l^{-1}$.

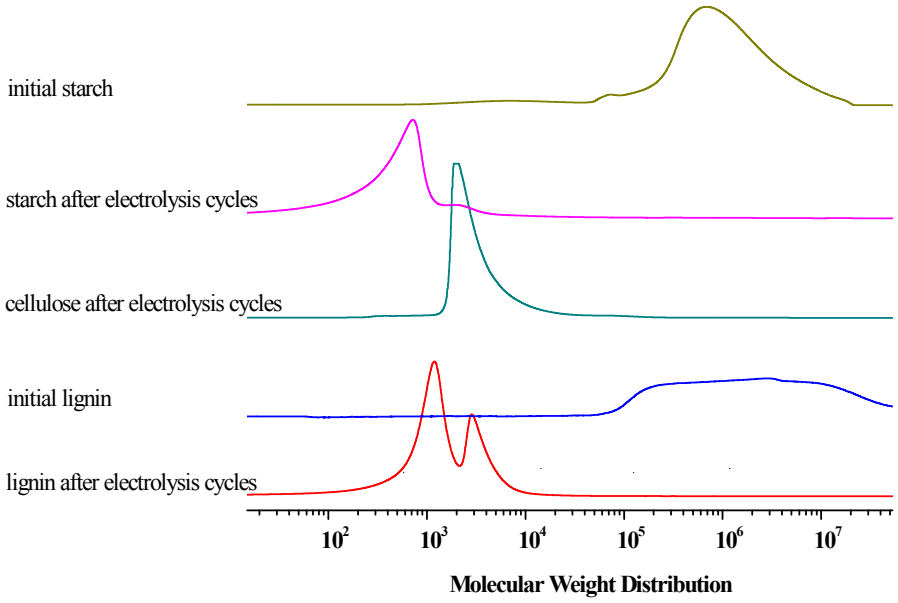



Figure S7 gel permeation chromatography of different biomass and the biomass after heating-electrolysis cycles with $PMo_{12}$. Initial starch was heated in DI water at 95 °C 30 min for GPC test, and lignin was dissolved in NaOH solution (pH 10).

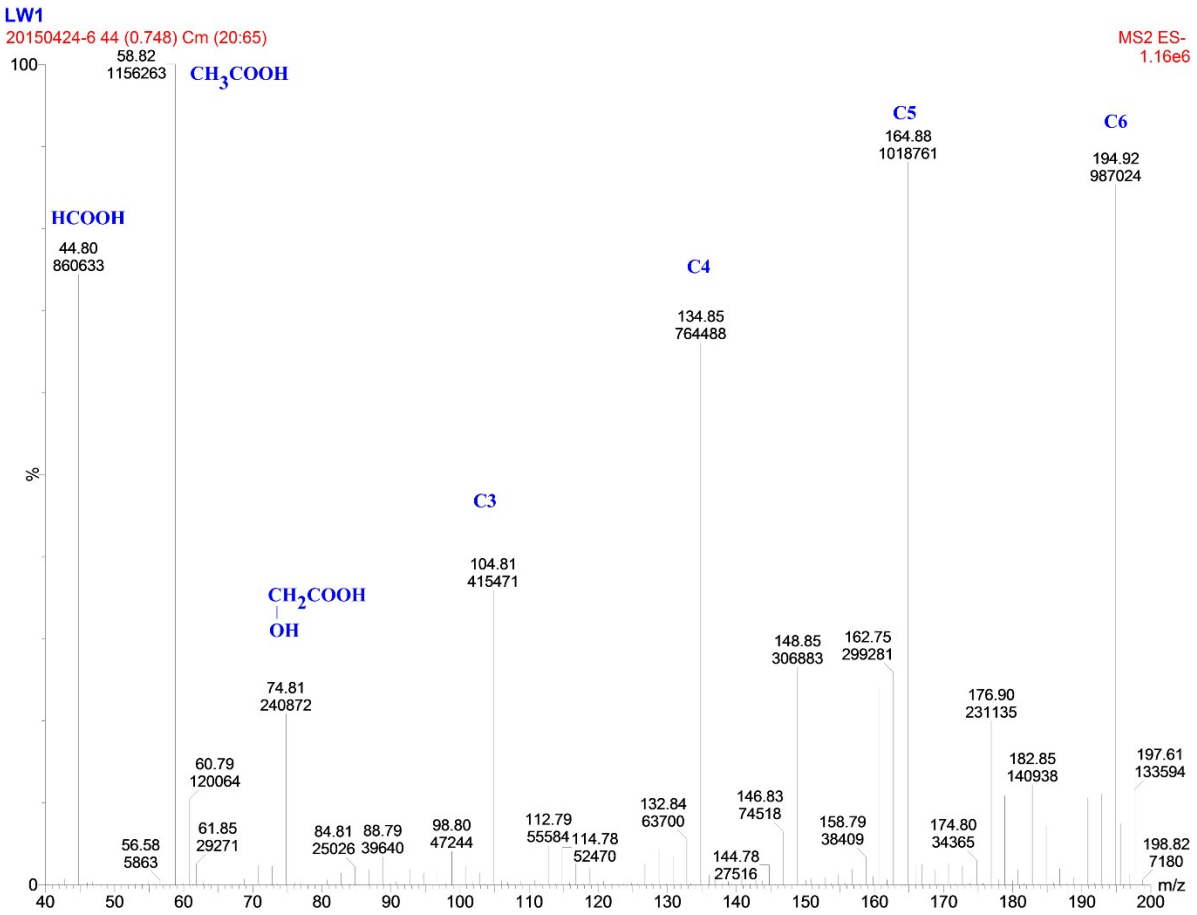
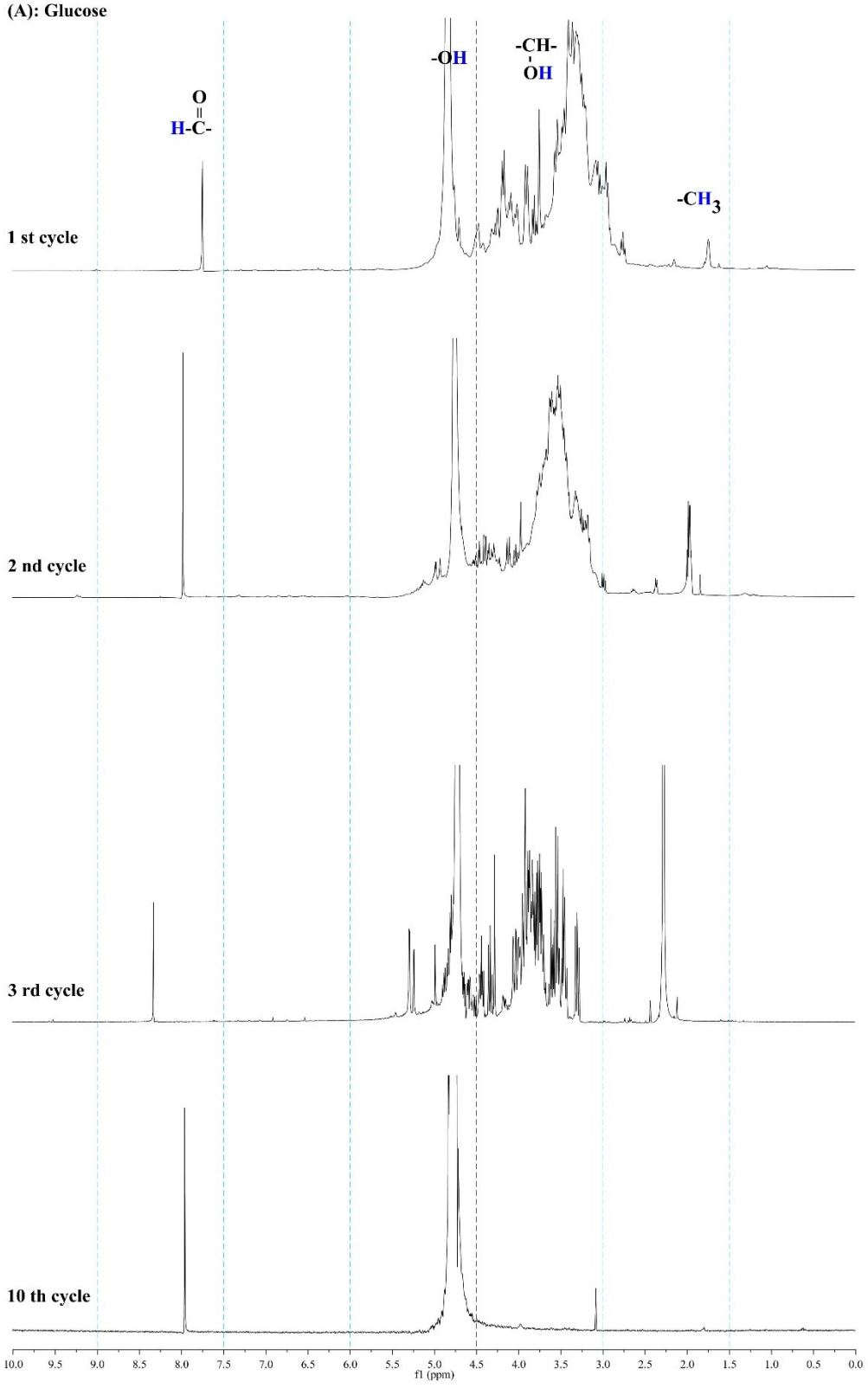
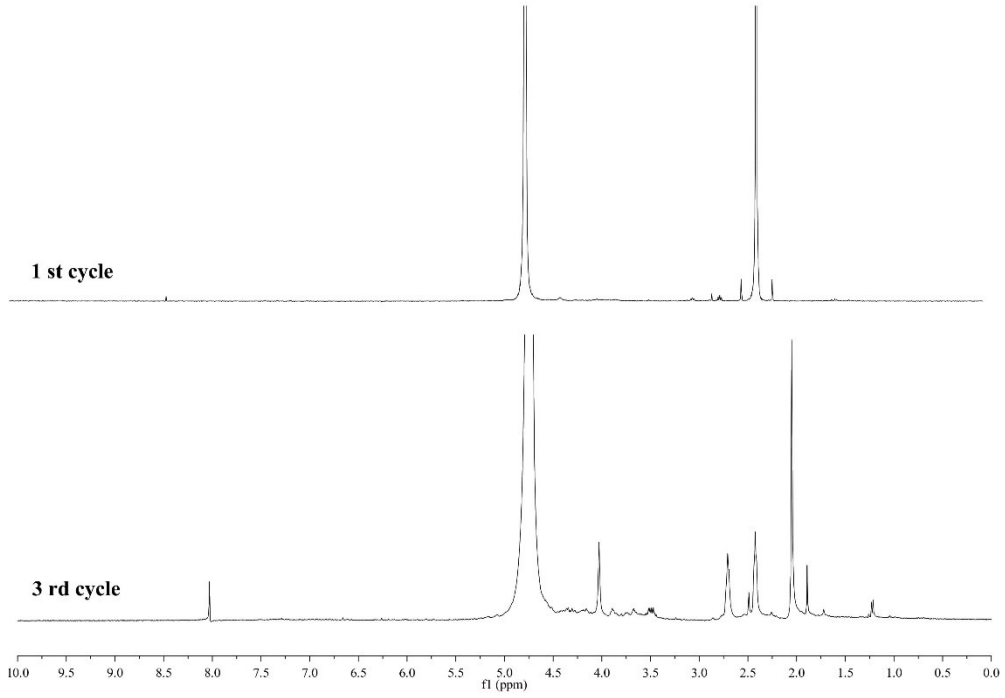


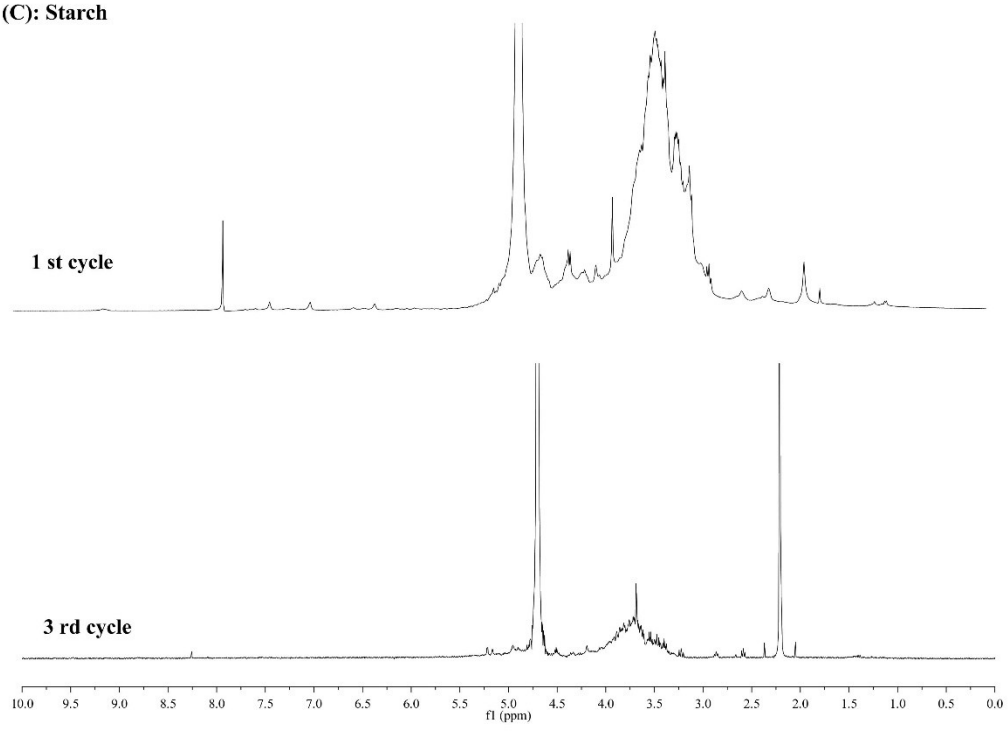

Figure S8 Mass spectrum of oxidation products of glucose. After several oxidation and electrolysis, the products were analyzed by HPLC-MS. Before the test, the sample was pretreated by adding CsCl to separate $PMo_{12}$.


(A): Glucose
-OH
-CH-
OH
O
H-C-
-CH3
1 st cycle
2 nd cycle
3 rd cycle
10 th cycle
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

**(B): Cellulose**



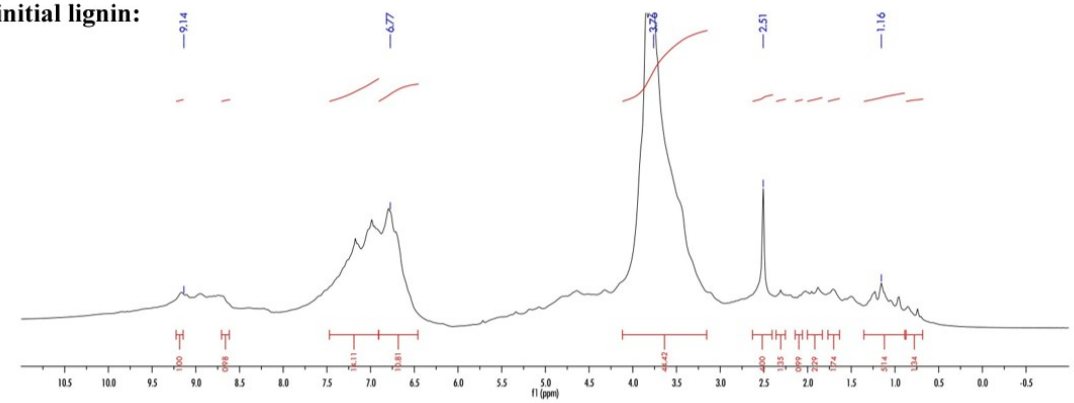

**(C): Starch**



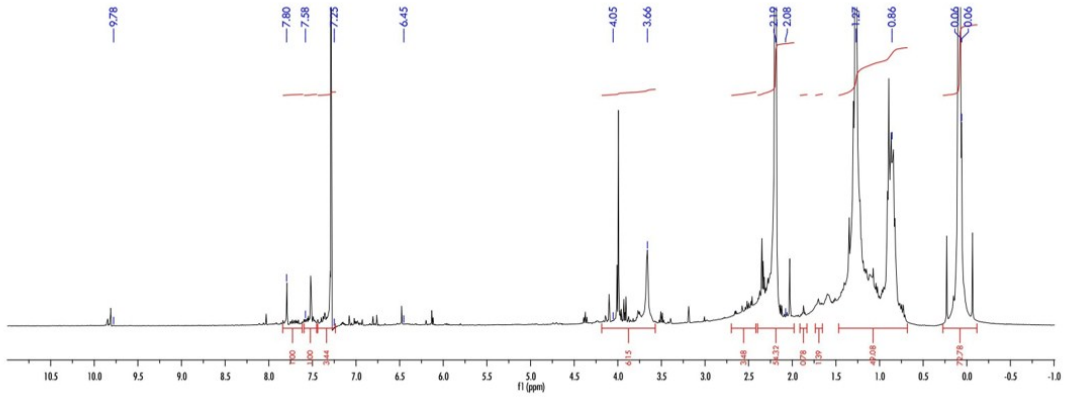
**(D)**

**$^{1}$H NMR**

**initial lignin:**

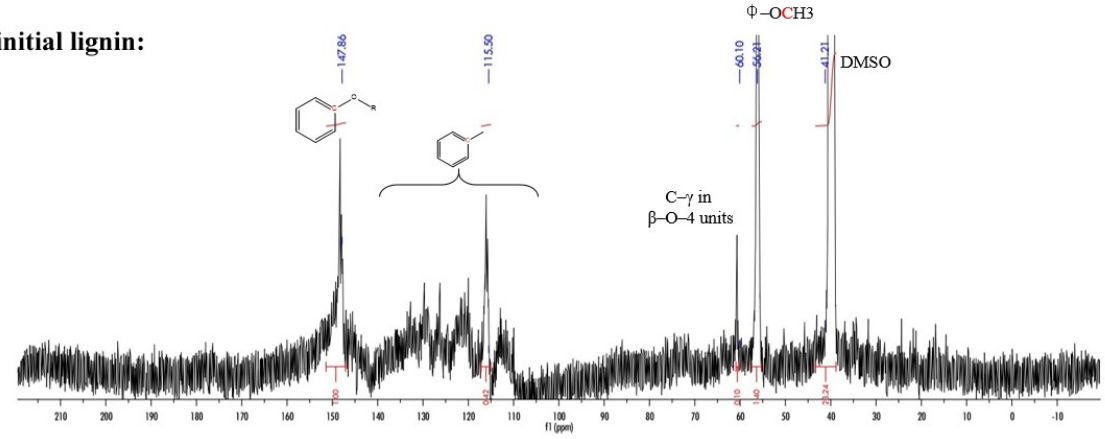



**After electrolysis cycles:**



**$^{13}$C NMR**

**initial lignin:**




**After electrolysis cycles:**

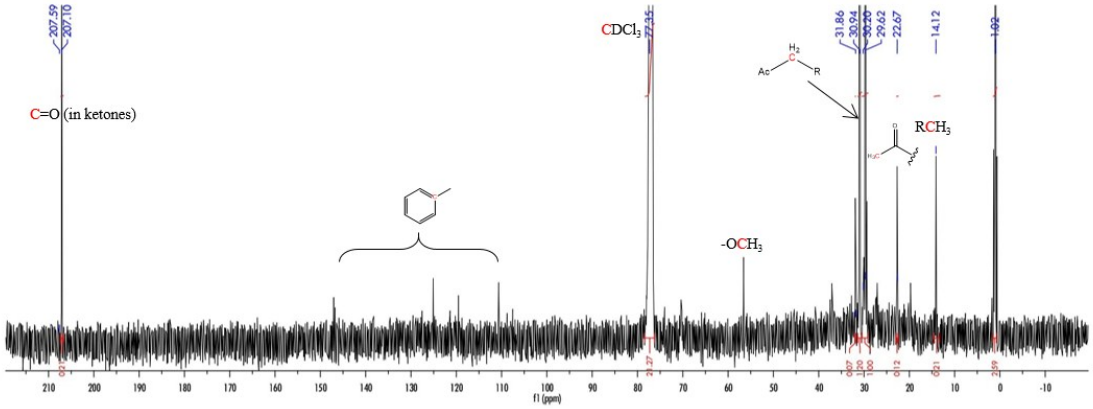



Figure S9 (A) $^{1}$H NMR of oxidation products of glucose in the electrolysis cycles (solvent $D_2O$); (B) cellulose; (C) starch; (D) $^{1}$H NMR and $^{13}$C NMR of initial lignin and oxidation products after electrolysis cycles (solvent DMSO-$d_6$).

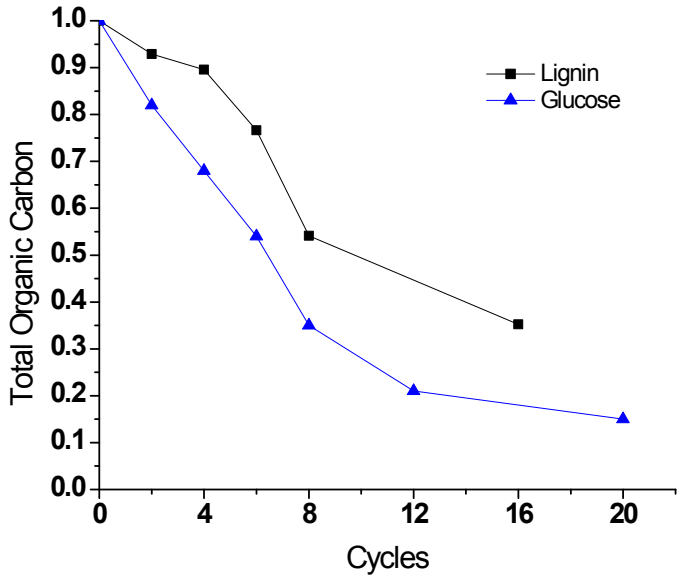



Figure S10 Total organic carbon (TOC) analysis of lignin or glucose-$PMo_{12}$ solution in repeated heating-electrolysis cycles. Reaction conditions: $PMo_{12}$ 0.3 mol $l^{-1}$, glucose (or lignin) 10 g $l^{-1}$, total volume of solution 20 ml; heating at 100°C for 6 hours for every cycle.

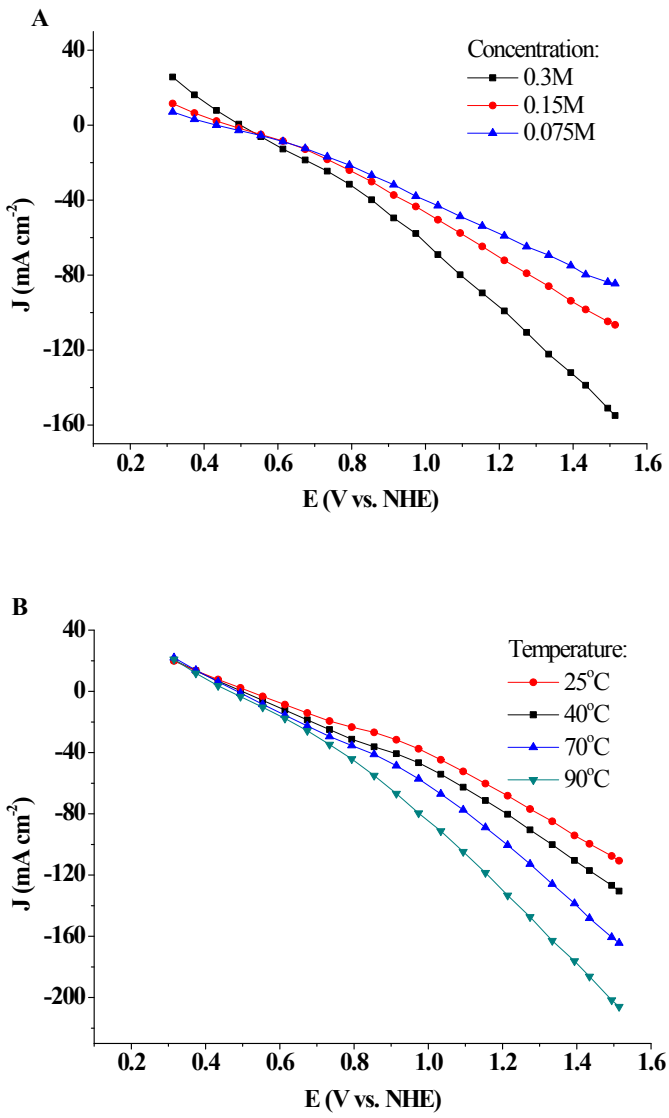



Figure S11 (A) Linear potential sweep curves of $PMo_{12}$ (reduction degree 3.1)-glucose soution (25 °C) in different concentration; (B) Linear potential sweep curves of $PMo_{12}$ (0.3 mol $l^{-1}$; reduction degree 2.8)-glucose soution at different temperature.

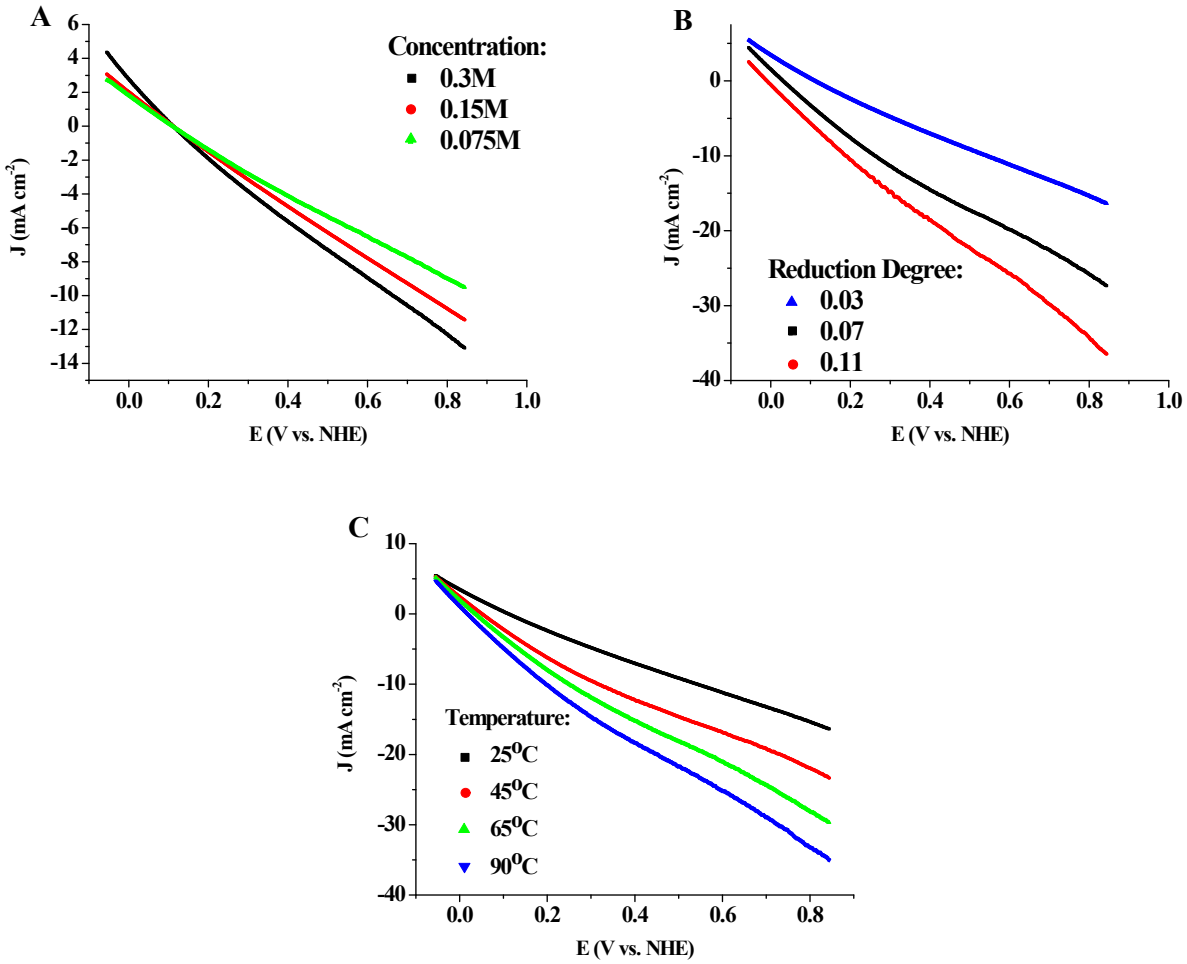



Figure S12 (A) Linear potential sweep curves of $SiW_{12}$ (reduction degree 0.11)-glucose soution (25 °C) in different concentration;(B) curves of $SiW_{12}$ (0.3 mol $l^{-1}$)-glucose soution (25 °C) with different reduction degree; (C) curves of $PMo_{12}$ (0.3 mol $l^{-1}$; reduction degree 0.11)-glucose soution at different temperature.

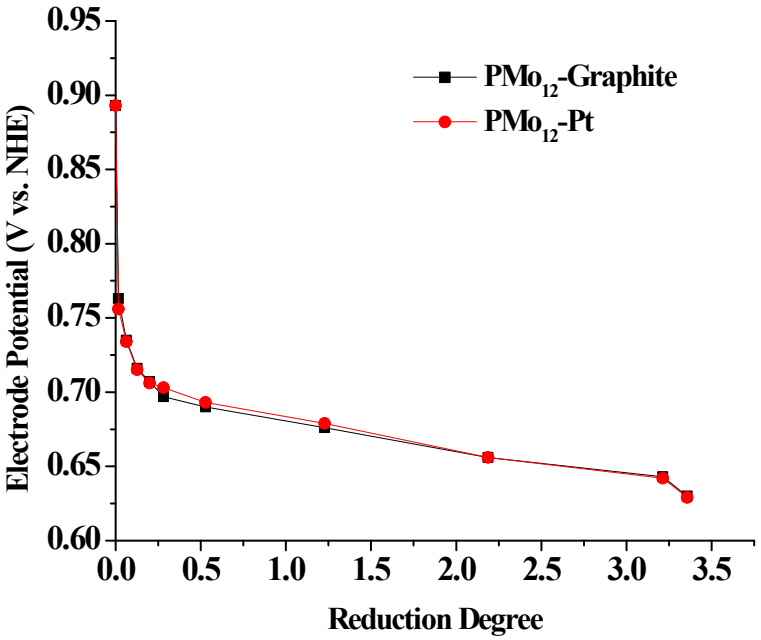



Figure S13 Electrode potential (25 °C) of $PMo_{12}$ solution on graphite and Pt electrode at different reduction degree.

**Table S1.** Composition analysis of emission gas from anode side by GC*

| Results | Concentration (mol%) |
|---|---|
| Oxygen | 0 |
| Nitrogen | 99.8 |
| Carbon monoxide | 0 |
| Carbon dioxide | 0.2 |

* The emission gas was collected from the anode side of electrolyzer in a continuous running. Air in the anode side was purged out by pure $N_2$ gas before experiment. Then the anode side was pumped with glucose-PMo12 solution (2 mol l-1 and 0.3 mol l-1 respectively). The electrolysis current density was 200 mA $cm^{-2}$ and simultaneously the glucose-$PMo_{12}$ was heat at 95 °C for continuous oxidation of glucose. No oxygen gas was detected in the final emission gas, which indicates water electrolysis did not occur.