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Biomass is a sustainable source for hydrogen production. Although thermochemical (pyrolysis and gasification) has been practically applied to produce hydrogen, the process requires high temperature and expensive catalysts. The presence of mixture gases in the hydrogen product is another problem. Biological (biophotolysis, water–gas shift reaction and fermentation) processes can produce hydrogen from biomasses, but the efficiency is low. Electrolysis technology can produce pure hydrogen at low temperature, but the current technology cannot utilize polymeric biomass directly. Furthermore, the noble metal catalysts used in current electrolysis process are easily poisoned by contaminants existing in raw biomass. Herein, we report an electrolysis approach for directly producing hydrogen from almost all native biomasses by using polyoxometalate (POM) solution as both catalyst and charge carriers. The catalytic redox reaction occurs in the solution but not on anode surface. As a result, noble metal is no longer needed for anode. POM catalyst is robust and tolerant to most organic and inorganic contaminants. Therefore, chemical pretreatment is not necessary for native biomass. The electrolysis energy consumption is very low, which is only about 16.7% of the energy consumption of electrolysis of water.



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COMMUNICATION

High efficiency hydrogen evolution from native biomass electrolysis†

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A novel electrolysis approach for hydrogen evolution directly from native biomass, such as cellulose, lignin and even wood and grass powders, to hydrogen at low temperature is presented. Using aqueous polyoxometalates (POM) as catalyst at the anode, the raw biomass is oxidized and electrons are transferred to POM molecules by heating or light-irradiation. Protons from biomass diffuse to the cathode and are reduced to hydrogen. The electric energy consumption could be as low as 0.69 kWh per normal cubic meter of H₂ (Nm³ H₂) at 0.2 A cm⁻², which is only 16.7% of the energy consumed for reported water electrolysis. Unlike the traditional electrolysis of alcohols, a noble-metal catalyst is not required at anode.

Hydrogen is the most abundant element in the universe, and also the cleanest fuel on Earth^{1, 2}. Because hydrogen has the highest energy density of all fuels (143 kJ kg⁻¹), it is suggested that 1 kg of hydrogen can effectively replace 2.63 kg of gasoline³. Hydrogen combustion emits only water vapor without carbon emissions. However, 96% of the global demand for hydrogen is currently produced from petroleum reforming and coal gasification³. Because biomass is one of few currently available renewable energy sources, a biomass based route for sustainable hydrogen generation is highly attractive⁴.

Hydrogen production from biomass includes a variety of developing technologies including thermo-conversion, photoelectrochemical conversion, fermentation, and electrolysis⁵. Biomass thermo-conversion (e.g., gasification, pyrolysis and water/steam treatment etc.) presents a possible large-scale hydrogen production route from agricultural or forestry residues³, but there are also some technical barriers including low heat efficiency, poor catalysts durability and impurities in the product etc⁶. Photoelectrochemical (PEC) process and fermentation are promising approaches for hydrogen production from biomass and derivatives^{7, 8}.

However, the low hydrogen generation rate of PEC process and fermentation has still not been overcome yet so they are difficult to be practically adopted⁶. Electrolysis process provides a quick and convenient approach to produce pure hydrogen. Comparing to water electrolysis, biomass electrolysis generates hydrogen by substituting oxidation of biomass-derived fuels at anode for oxygen evolution reaction, which can significantly reduce the electric energy consumption required for hydrogen production.

Electrolysis of renewable biomass for producing hydrogen can be realized by two common technologies: proton exchange membrane electrolysis cell (PEMEC) and microbial electrolysis cell (MEC)⁹. Recently, the performance of PEMEC was highly improved using nanostructured noble-metal catalysts on the anode¹⁰. However, several issues still exist with the current technologies. The current PEMECs are limited to a few biomass-derived alcohols, such as ethanol, ethylene glycol and glycerol etc. Native polymeric biomass like starch, cellulose and wood-powder have not been directly used in PEMECs up to now because the noble-metal based catalysts cannot effectively catalyse the conversion reaction of polymeric biomass-molecules at low temperature. Even for ethanol, the simplest C-C bond alcohol, it could be electronically oxidized to acetic acid (-4e) in PEMEC, which means a very low hydrogen mole yield can be achieved. Completely oxidizing of 1 mol of ethanol (-12e) could produce 6 mol hydrogen; otherwise only 1/3 (2 mol) hydrogen could be obtained when it ended at the product of acetic acid. The performance deterioration also occurs because the noble-metal catalyst based anode is sensitive to some of intermediates such as CO, some sulphur compounds and other impurities formed during reaction. Moreover, as alkaline mediation is used in common PEMEC, NaOH is also consumed during the electrolysis process because organic acids are generated as the oxidation products. The alkaline mediation process adds to the cost of hydrogen production as well. Even though microbial electrolysis cell (MEC) can use different types of substrates ranging from organic acids to alcohols, microorganisms in MEC cannot directly utilize lignocellulosic biomass, an abundant renewable resource in the nature^{11, 12}. It has to be

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fermented firstly to convert to low-molecular-weight compounds or monosaccharides. In addition, slow hydrogen production rate and the limited lifetime hinder their application. Therefore, highly efficient hydrogen production directly from biomass is a valuable research objective but with great challenges.

Recently, we reported a direct biomass fuel cell that uses polyoxometalates (POM) as the catalyst to realize the biomass-to-electricity conversion at low temperature^{13, 14}. Polyoxometalates are water-soluble molecular metal-oxide clusters that have been used in photocatalytic water splitting^{15, 16}. In some advanced researches, POMs were used as electron-coupled-proton buffer in water electrolysis for decoupling hydrogen and oxygen evolution^{17, 18}. Herein, we present a novel chemical-electrolysis conversion (CEC) process utilizing polyoxometalates as both catalyst and electron-proton carrier for hydrogen generation directly from native biomass. In this process, raw biomass can be effectively decomposed via a chemical conversion by aqueous POM at low temperature and followed by electrolysis with very low electric energy input to generate hydrogen.

The chemical-electrolysis conversion process was conducted in a common PEMEC, which was schematic illustrated in Fig. 1A. The proton exchange membrane was sandwiched between a simple graphite-felt anode without coating any catalyst and a carbon cathode coated with Pt black catalyst (4 mg cm^{-2}) for hydrogen evolution (Experimental setup and details of graphite-felt anode are shown in the supplemental information Fig. S1). Before the electrolysis, biomass was mixed with solution of phosphomolybdic acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$, noted as PMo_{12}) that is one of the typical POMs (shown in Fig. 1 bottom (B)). Under either sunlight irradiation or direct heating, the biomass- PMo_{12} mixture gradually changed the colour from initial yellow to dark blue (shown in Fig. 1 bottom (C)), indicating the reduction of POM and oxidation of biomass. The electrolysis carried out by applying an electric potential to the anode and cathode (shown in Fig. 1 A). At the same time, the obtained biomass-POM solution was pumped into the anode and phosphoric acid aqueous solution (1 mol l^{-1}) was pumped into the cathode side of the electrolysis cell. During the electrolysis, the reduced POM was gradually electro-oxidized, and turned back to yellow; hydrogen bubbles released from cathode outlet, and was collected. When the reduced POM blue completely turned to yellow at the anode side (shown in Fig. 1 D), a chemical-electrolysis conversion cycle was completed. Experimentally, the biomass-POM solution could be irradiated or heated *in situ* with the circulation in the electrolyzer to generate hydrogen.

In order to understand the biomass-POM hydrolysis process, a control test was performed first with only phosphoric acid (1 mol l^{-1}) pumped through both the anode and cathode sides. As expected and shown in Fig. 2 A, there is no obvious current even when the applied potential was 1.1 V because the applied potential is lower than the standard potential of water electrolysis (1.23 V), and the oxygen evolution reactions has a large over-potential over graphite electrode in phosphoric acid. This was further confirmed by the cyclic voltammetry of

graphite electrode in H_3PO_4 solution and the I-V curve in an extended applied potential range (shown in Fig. S2). When the electron donor, for example, glucose, was introduced into H_3PO_4 solution, it can be observed that the electrolysis current was still very low (Fig. 2A). This is reasonable because no noble-metal catalyst was loaded on the carbon anode. However, when simply heated blue biomass- PMo_{12} solution was pumped through the anode, electrolysis current sharply increased after applied potential was raised over 0.6 V (Fig. 2A), and hydrogen gas bubbles were clearly observed at the cathode side. Current density up to 0.45 A cm^{-2} was measured at applied potential 1.0 V by electrolyzing of native starch powder. This is much higher than the value of electrochemical conversion of ethanol alcohol in common PEMEC (0.2 A cm^{-2} at applied potential 1.0 V)^{19, 20}, even though no noble-metal catalyst was used on the anode in our study. After 2 hours electrolysis, the solution colour turned back to yellow (Fig. 1 bottom (D)), indicating the POM anions were oxidized to their original state.

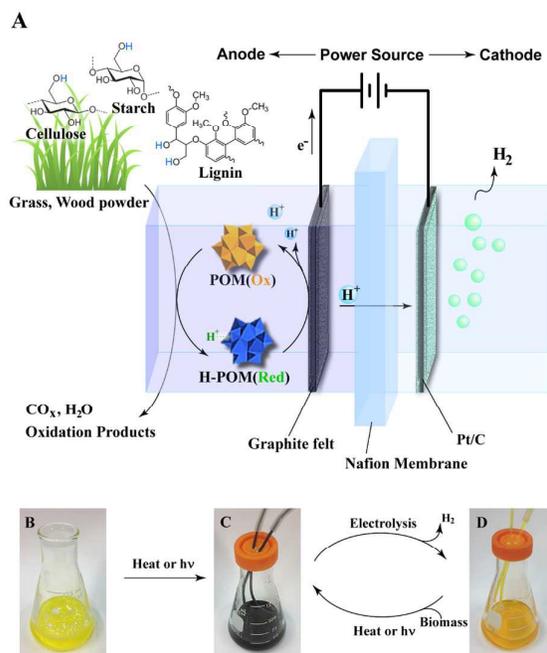


Fig. 1 (A) Schematic illustration of the chemical-electric conversion process. Anode is a simple graphite-felt electrode; cathode is a gas-diffusion electrode loaded with Pt black catalyst (4 mg cm^{-2}). (B) Solution of POM-biomass before heating or light irradiation. (C) The colour change of biomass-POM mixture after heating. (D) The biomass-POM solution after electrolysis for hydrogen production.

Not only native starch powder but also several other types of biomass, including glucose, lignin suspension, cellulose powders, switchgrass, poplar wood powder and fresh algae were directly used for hydrogen production, as shown in Fig. 2 A and B. It should be noted that the native biomass used in this study were only mechanical grounded without any chemical pre-treatment. The biomass powders actually were particle suspensions in the POM solution at the beginning, and they gradually dissolved after reacting with PMo_{12} at elevated

temperature (90–100 °C). These experiments demonstrate, for the first time, the successful conversion of raw biomass into hydrogen at low temperature.

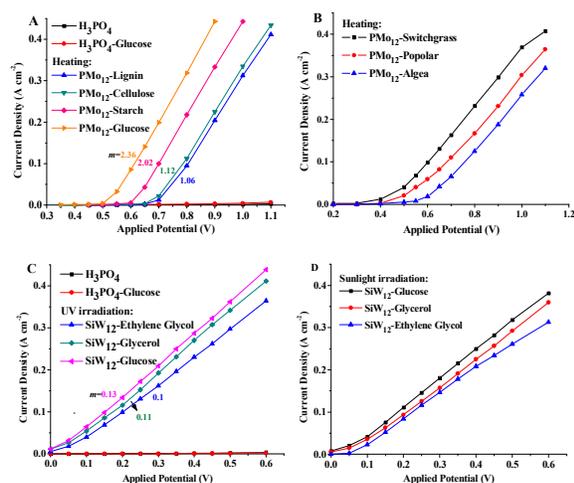


Fig. 2 (A) (B) Polarization curves of PMo_{12} (0.3 mol l^{-1}) and biomass solution (fed with anode side) preheated at $100 \text{ }^{\circ}\text{C}$ for 2 hours. Cathode side is pumped with 1 mol l^{-1} H_3PO_4 solution. (C) Polarization curves of SiW_{12} (0.3 mol l^{-1}) and alcohols (2 mol l^{-1}) pre-irradiated under UV-light (irradiation density 60 mW cm^{-2} ; irradiation area 15.8 cm^2 ; solution volume 10 ml) at room temperature for 1 hours. (D) Polarization curves of the solution pre-irradiated under sunlight (irradiation density 6.16 mW cm^{-2} ; irradiation area 15.8 cm^2 ; solution volume 10 ml) for 6 hours. Values of reduction degree (m) of PMo_{12} and SiW_{12} in different solutions are noted. The electrolysis temperature is $80 \text{ }^{\circ}\text{C}$.

Besides heating induced redox reaction, light can also be used to induce the redox reaction between POM and biomass because POM is a photosensitive catalyst^{21,22}. Therefore, light-drive electrolysis of biomass was also performed in this study by mixing PMo_{12} and bio-derived alcohols such as glycerol and glucose under irradiation of AM-1.5 solar simulator (experimental conditions shown in Fig. S3). This process was promoted by using silicotungstic acid ($\text{H}_4\text{SiW}_{12}\text{O}_{40}$ noted as SiW_{12}) that has strong photocatalytic ability under short-wavelength light irradiation. Fig. 2C shows the electric performance by using bio-alcohols- SiW_{12} mixture after UV-irradiation. The results indicated that even at 0.1 V applied potential, about 50 mA cm^{-2} electrolysis current and significant hydrogen evolution at the cathode was observed. To the best of our knowledge, this is the lowest electrolysis voltage that shows

remarkable hydrogen generation in the literature. The electric energy consumption drops to $0.69 \text{ kWh Nm}^{-3} \text{ H}_2$ at a current density of 0.2 A cm^{-2} . Considering the reported alkaline water electrolysis, 1.8 V potential and the energy of $4.3 \text{ kWh Nm}^{-3} \text{ H}_2$ was generally required²³, which suggests 83.3% electric energy could be saved by using light-induced alcohols- SiW_{12} solution. Even for reported methanol or ethanol-water electrolysis, the energy consumption is usually in the range of $1.5\text{--}2.0 \text{ kWh Nm}^{-3} \text{ H}_2$ ^{20,24}, which is still ~ 2.8 times higher than our approach. Not only UV light but also sunlight could induce electron transfer from biomass to SiW_{12} . As shown in Fig. 2 D, sunlight irradiated biomass- SiW_{12} solutions have similar electric performance as UV irradiation, which depends actually on the reduction degree of the POM. Because solar energy is the cleanest and most abundant renewable energy source, using solar-induced redox reaction of native biomass in the presence of POM could provide practical route to significantly reduce the cost and energy consumption in hydrogen production.

As shown in Fig. 2, it seems that the onset potential (the point at which the electrolysis current suddenly increases) depends on the type of biomass. For example, glucose and starch solution have small onset potentials because glucose and starch are easily oxidized and hydrolysed by POM. But cellulose and lignin have opposite situations due to the rigid crystalline structure in cellulose and achromatic rings in lignin. However, the actual reason affecting the onset potential is the reduce degree of the POM after reacting with biomass under either heating or light irradiation. Even under the same experimental condition, different biomasses could result in different reduction degree of POM because the redox reaction between biomass and POM depends on the chemical structure of biomass. The reduction degree (noted as m , shown in Fig. 2) of POM was defined as the average number of electrons (in moles) that were transferred from the biomass to one mole of POM anion. The absorbance at the wavelength of 700 nm of reduced POM was utilized for reduction degree determination, because the linear relationship between the absorbance at 700 nm and reduction degree was demonstrated (shown in Fig. S4). The reduction degree of POM is our concern in electrolysis because actual electric oxidation on the anode is POM anions rather than biomass molecules (demonstrated by cyclic

Table 1 Comparison of different electrolyser for hydrogen evolution from biomass

Electrolyser	Fuel	Electrolyte	Temperature ($^{\circ}\text{C}$)	Current density (mA/cm^2)	Applied potential (V)	Power consumption ($\text{kWh/Nm}^3\text{H}_2$)	Ref.
Photoelectrochemical cell	Alcohols and saccharides	KOH or H_2SO_4	Ambient	0.05-2.55	0-1.23		7, 25
PEM alcohol electrolyser	Methanol, ethanol, glycerol	Water, KOH or H_2SO_4	60-80 $^{\circ}\text{C}$	100	0.45-0.8	1.08-1.91	20, 24, 26, 27
				200	0.5-1.2	1.20-2.87	
				500	0.6-2	1.44-4.79	
CEC cell	Alcohols, starch, cellulose, lignin, wood powder	Aqueous POM	Ambient to 80 $^{\circ}\text{C}$	100	0.15-0.7	0.36-1.67	This work
				200	0.28-0.8	0.67-1.91	
				500	0.6-1.2	1.44-2.87	

voltammetry shown in Fig. S5). The higher reduction degree the POM has, the lower onset potential is required in the electrolysis, and more electrolysis energy could be saved. This mechanism is different from noble metal catalyzed alcohol electrolysis in which the redox reaction of alcohol molecules occurs on the Pt loaded anode surface rather than in the solution. Therefore, the electric performance in this study not directly related to the chemistry of biomass although biomass chemistry is one of the important factors affecting the biomass-POM reaction kinetics.

In order to test the stability of the hydrogen evolution using biomass-POM electrolysis device, continuous tests running at constant-current densities of 50, 100 and 200 mA cm⁻² were performed under the conditions of both heating (by feeding with glucose-PMo₁₂ solution) and UV-irradiation (by feeding with glucose-SiW₁₂ solution). At the same time, the produced H₂ gas was measured. As shown in Fig. 3, the potential was very stable during the process of 24 ml H₂ generation. The steady performance depends on a stable electron capturing from biomass by POM. The redox reaction rates between different types of biomass and POM were determined under heating, UV and actual sunlight irradiation (shown in Fig. S6). Actually, the biomass-POM reaction rate strongly relies on the conditions such as irradiation intensity, irradiation area, temperature and concentration etc., but results show that the reaction rates are sufficient for the continuous hydrogen production. Theoretical yield of H₂ gas during the constant-current electrolysis was calculated according to the Faraday's laws (shown in Fig. 3 B and D). The average Faraday efficiency (ratio of measured to theoretical yield of H₂) is 96.74%, which indicates it has a high efficient electrons transfer in the overall process from biomass to H₂.

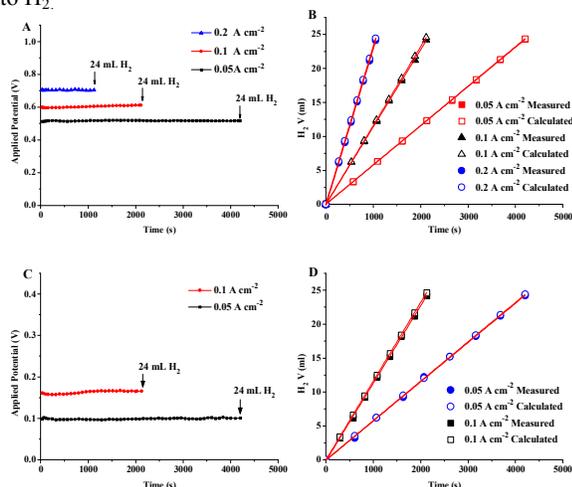
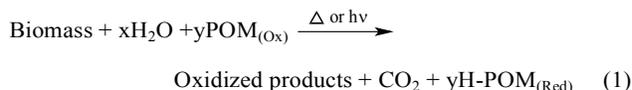


Fig. 3 Variation of applied potential vs. time during constant current-density (0.05, 0.1 and 0.2 A cm⁻²) electrolysis of H₄PMo₁₂O₄₀ (PMo₁₂)-glucose solution simultaneously with heating (electrode area 1 cm²). (B) H₂ volume collected during the PMo₁₂-glucose constant current-density electrolysis at different time and the calculated value according to Faraday's law. (C) Constant current-density (0.05 and 0.1 A cm⁻²) electrolysis of

H₄SiW₁₂O₄₀ (SiW₁₂)-glucose solution simultaneously under UV-irradiation (electrode area 1 cm²). (D) Faraday efficiency calculation during the constant current-density electrolysis of SiW₁₂-glucose.

It is of interest to know what the final products in the system are and how much hydrogen can be released from the biomasses. The final products depend on the chemistry of the biomass, the reaction temperature and time, the type of POM and its concentration. Although the actual redox reactions and the reaction products are complicated, it was confirmed in this study that the high molecular weight native biomasses were first depolymerized to low molecular weight derivatives. Gel permeation chromatography (GPC) was used to demonstrate the decomposing of polymeric biomass into a series of small molecular-weight substances (shown in Fig. S7). Oxidized organic species in the electrolyte solution were analysed by HPLC-MS, GC-MS, ¹H and ¹³C NMR spectroscopy (shown in Fig. 4, S8 and S9). The major oxidation residues of glucose, cellulose and starch are formic acid, glycolic acid and acetic acid. The emission gas from the reaction was collected and analysed using gas chromatography (GC) and CO₂ was the only gas emitted from the solution reactions (supplementary information Table 1). When glucose was used as the feeding raw material, the Total Organic Carbon (TOC) analysis showed that 80% weight of the initial glucose was consumed to CO₂ after 20 repeated oxidation and electrolysis cycles (shown in Fig. S10). Alternately, when lignin was used, some aromatic compounds, such as vanillin and methyl vanillate were founded in the solution, and CO₂ was found in the emission gas. If the biomass-POM reactions were induced by light irradiation rather than heating, the vanillin and methyl vanillate could further be converted to CO₂.

Based on the electrical characterizations and chemical analyses, the principle of this chemical-electrolysis conversion process can be proposed. The conversion process starts with the oxidation of biomass by POM in solution under the condition of heating or light irradiation, to form a reduced POM complex (H-POM_{Red}). At the same time, water may also play as a proton donor in the biomass oxidation by POM⁵, as shown in equation (1):



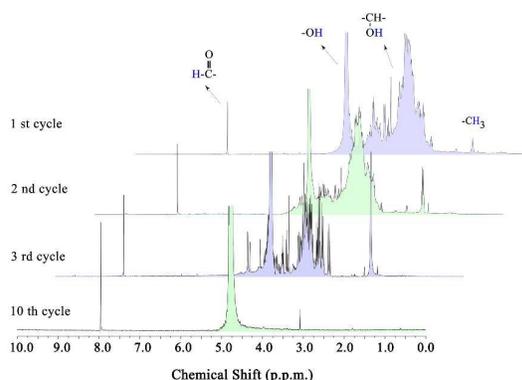


Fig. 4 ^1H NMR spectrum of glucose- $\text{H}_3\text{PMO}_{12}\text{O}_{40}$ (PMO_{12}) solution in repeated electrolysis cycles.

When POM accepts the electrons from biomass, the valency of metal ions (Mo^{6+} or W^{6+}) changed into a low valency state (Mo^{5+} or W^{5+}), which leads to a drop of the electrode potential of the POM solution. The electrode potentials with different reduction degrees were investigated using a graphite electrode immersed in POM solution, which was shown in Fig. 5A. With the reduction degree of SiW_{12} increased from 0 to 0.12, the electrode potential decreased from 0.65 V to near 0 V (Vs. Normal Hydrogen Electrode (NHE)). For PMO_{12} , the electrode potential dropped about 0.3 V after the reduction degree increased to 3. These results indicate the reduced POM complex can be readily oxidized on anode when an electric potential was applied. The linear potential sweep curves (shown in Fig. 5B) clearly illustrate that high reduction degree POM requires a low applied potential for electro-oxidation and produces a large anodic current density at the same applied potential. Many factors may affect the anodic currents such as the reduction degree, temperature and the total concentration of POM anions etc. The detail experiments of linear potential sweep reveal that the reduction degree and temperature are significant factors that will profoundly promote the electrolysis performance (shown in Fig. S11 and S12).

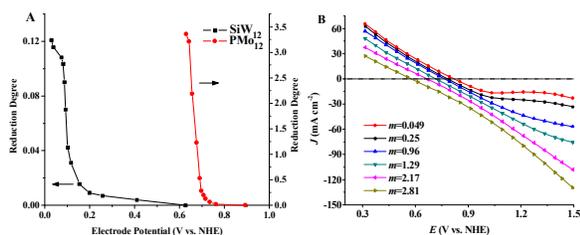
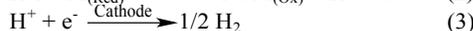


Fig. 5 (A) Electrode potential (25 °C) of PMO_{12} and SiW_{12} (0.3 mol l^{-1}) on graphite at different value of m . Pt wire was used as counter electrode and a saturated calomel electrode (SCE) was used as reference electrode. (B) Linear potential sweep curves of PMO_{12} (0.3 mol l^{-1})-glucose solution (25 °C) at different reduction degree in a three electrode compartment using a polished graphite rod as working electrode.

By applying an electric field, the reduced POM complex releases an electron to the anode electrode, and a proton into the electrolyte solution, as shown in equation (2). This electron transfer process does not require the assistant of noble-metal catalysts (demonstrated by Fig. S13). Therefore, different from

the traditional PEM electrolysis cell, the anode in our biomass electrolyzer was made of simple graphite-felt without noble-metal catalysts.

The released proton diffuses to the cathode side through the proton-exchange membrane and combined with the electron that comes from the anode side under applied electric field. Finally H_2 produced, shown in equation (3):



In summary, a new route for high efficient chemical-electric conversion (CEC) of biomass to H_2 was reported. Although it has been known that adding alcohols in PEMEC can reduce the split energy, the sluggish kinetics of the alcohol oxidation on electrode leads to a high over-potential and the high cost of the noble-metal catalyst used in traditional electrolysis limit their commercial application. Different from the traditional PEMEC method, we reported a new route here that biomasses were directly oxidized by POM in the aqueous solution but not on the anode electrode surface. As a result, raw biomass without chemical pre-treatment and purification with a form of suspended solid powder or soluble polymer solution can be directly used for hydrogen production with the electrolysis method. Reacted with POM in solution, biomass is degraded and continuously oxidized into small derivatives, and part of the ultimate product in the oxidation could be CO_2 , which indicates a high utilization of biomass. The electron transfer from biomass into POM can be promoted by simple heating or sunlight irradiation. Therefore, the solar energy and chemical energy of biomass are transformed and stored in the form of reduced POM complex in the electrolyte solution. The reduced POM has a low applied potential and it can be readily reoxidized on a carbon anode. This leads to a large drop of applied potential during the electrolysis, and therefore a large amount of electric energy can be saved by electrolysis of biomass-POM solution. The POM ions also play as the electron-proton carrier that captures electrons from biomass and protons from water and biomass. Therefore, a complete noble metal free carbon electrode could be adopted as the electrolysis anode. In addition, different from the noble-metal catalysts applied in traditional PEM electrolysis cell, POM catalyst is tolerant to most organic and inorganic contaminants²⁵, and the cost of POM is very low. Because POMs are robust and self-healing²⁵, they can be reused in this chemical-electrolysis conversion. Borrás-Almenar et al. indicated that for the reaction mixture containing substrate and POM catalyst, hundreds of thousands of turnovers are possible.²⁶ If the biomass can be completely decomposed to CO_2 , biomass is the only material to be added to the system, and a completely reuse of POMs can be realized. The direct use of raw biomass, the noble-metal catalyst free anode and the very low electric energy consumption demonstrate a promising route for H_2 production in this study.

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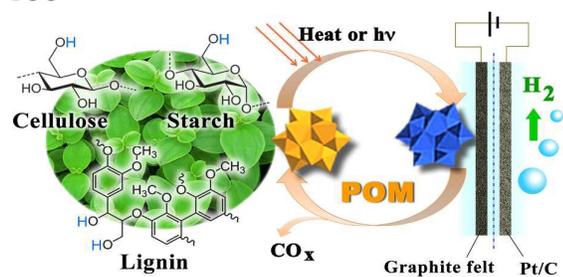
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A novel approach for directly producing hydrogen using electrolysis method from almost all native biomasses was reported.