Artificial photosynthesis of oxalate and oxalate-based polymer by a photovoltaic reactor

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A photovoltaic reactor was designed for artificial photosynthesis, based on the reactions involved in high energy hydrogen atoms, which were produced from water electrolysis. Water and CO2, under the conditions studied, were converted to oxalate (H2C2O4) and a polymer. This was the first time that the oxalate and oxalate-based polymer were produced from the artificial photosynthesis process.

Results

The photovoltaic reactor for artificial photosynthesis was designed as Fig. 1.

The photovoltaic reactor consisted of a solar panel, an accumulator and an electrolytic cell. The solar panels were used to absorb solar energy, which was then converted into electric energy. The electrolytic cell was the sites of reactions, where the high energy hydrogen atoms and oxygen were produced by electrolysis of water. Then oxalate and polymer were subsequently synthesized.

The reactor was operated under the conditions studied for 480 hours, thereby a produced solution were obtained. Then the solution was analyzed by high performance liquid chromatography (HPLC) (Fig. 2), in which oxalate concentration was 17.32 g/L. For the 600 ml solution, total of 10.39 g of oxalate was obtained. The produced solution was treated in the following order: 1) strong acidic cation-exchange resin, 2) strong basic anion-exchange resin to remove the generated oxalate and other electrolytic compounds, and finally a neutral solution was obtained. The neutral solution thus obtained was concentrated and dried, yielding 0.76 g.
neutral solid product, which was a transparent or translucent solid, shown in the supplementary figure 1 (S. Fig. 1).

The neutral solid product was analyzed by a gel permeation chromatography (GPC). The GPC spectrum contains two distinct peaks at 11.92 and 19.04 min, which accounted for 86.6% and 13.4%, respectively of the total peak area (S. Fig. 2). Based on the molecular weight calibration from globular proteins, the weight-average molecular weight (Mw) of the product at 11.92 min was $2.37 \times 10^5$ g/mol (Mw). The average molecular weight for the product at 19.04 min was 191.56 g/mol (S. Fig. 3 and 4). Therefore, the neutral solid product was regarded as a polymer.

To evaluate the performance efficiency of the reactor, the current efficiency, the electronic energy consumption efficiency and the cathode plate area efficiency were investigated. The current efficiency ($E_i$) is the ratio of the actual mass of special product ($M_i$) to the theoretical mass ($M_{th}$) of that product liberated according to Faraday’s law, %; expressed as equation (1). The electronic energy consumption efficiency ($E_{EEC}$) is the actual mass of special products ($M_i$) divided by the electronic energy consumption (EEC), g/kwh; expressed as equation (2). The cathode plate area efficiency of ($E_{CPA}$) is the actual mass of special products ($M_i$) divided by the area of cathode plate (CPA) and time (t), g/(m$^2$. h); expressed as equation (3).

Figure 1 | The photovoltaic reactor. The photovoltaic reactor consists of a solar panel, an accumulator and an electrolytic cell. Which electrolytic cell consists of an anode chamber, an anode plate and cathode plate. And a 2.5 μm micro porous membrane of PTFE was used as the separation membrane.

Figure 2 | The HPLC spectrums for the produced solution. It is the HPLC spectrum of the produced polymer, in which results show the oxalate absorption peak.
Under the conditions studied, the current efficiency of the reactor was about 18.4% for oxalate and 5.18% for the polymer. The electronic energy consumption efficiency was 123.69 g/kWh for oxalate and 9.05 g/kWh for the polymer. The cathode plate area efficiency was 17.32 g/(m² h) for oxalate and 1.27 g/(m² h) for the polymer.

The elemental composition of the polymer is (wt%): 40.90% as carbon, 54.53% as oxygen and 4.55% as hydrogen. So, the formula of polymer is expressed as C₈H₁₀.₇O₈. Based on the NMR results, the proposed structure of the polymer was given in Fig. 3. The polymer is made of oxalate, glycol and α-hydroxyl acetic acid.

Shown in Fig. 3, except the peak of solvent (D₂O, δ 4.70), there are three different hydrogen atoms in the ¹H NMR spectrum. Those at δ 3.225, 3.635, 3.745 and 4.035, noted as Hₐ, connected with C atoms at δ 62.29, may be assigned to CH₂ groups (S. Fig. 5 and 6)¹³–¹⁶. The peak at δ 8.544, noted as Hₐ, not connected with any C atoms (S. Fig. 6), is assigned to CH group (S. Fig. 5 and 6)¹⁶. The peak at δ 3.892, noted as H₈, connected with H atoms of δ 3.225–4.035, is assigned to CH₂ group (S. Fig. 5 and 6)¹⁶. The peak at δ 2.007, not connected with any C atoms, and out of the range of active H (S. Fig. 6), can be regarded as an interference peak.

The reaction mechanisms are explained as follows: The high energy hydrogen atoms produced by water electrolysis are attached on the surface of the cathode plate; provisionally are presented in the form of M–H. Subsequently, reaction between M–H and M–H (or H₃O⁺) takes place, producing hydrogen²⁸.

The reaction ability of the high energy hydrogen atom is strong because of the high energy level, which Gibbs free energy (DG) is 2206.5 kJ/mol at the statute of temperature of 298 K, atmosphere. Therefore, when other substrates touch the cathode plate, reactions between substrate and the high energy hydrogen atoms should take place; produce new hydrogenated products, as described in Equation (7).

The proposed structure of the polymer was further confirmed by Fourier transform infrared spectrometer (FTIR) and mass spectrometry (MS) results. There are five characteristic peaks in the FTIR spectrum. They are assigned to O–H, CO₂, C–O, and H–C–H (Fig. 5). These functional groups are consistent with the proposed polymer structure. Shown in Fig. 6 are the MS results, there are eight fragments that were less than 438 m/z, and all of them can be found in the proposed polymer structure.

Discussion

The reaction mechanisms are explained as follows: The high energy hydrogen atoms produced by water electrolysis are attached on the surface of the cathode plate; provisionally are presented in the form of M–H. Subsequently, reaction between M–H and M–H (or H₃O⁺) takes place, producing hydrogen²⁸.

H⁺ + M + e⁻ → M–H + H₂O (4)(Volmer)

M–H + M–H → 2M + H₂ (5)(Tafel)

M–H + H₃O⁺ → M + H₂ + H₂O (6)(Heyrovsky)

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Because oxalate is the main product and the polymer comprise the groups of oxalate, glycol and α-hydroxyl acetic acid. At the same time, CO₂, carbonic acid, high energy hydrogen atom and glyoxal (S. Fig. 7 and 8) exist in the system. The reaction pathways are suggested as Fig. 7.

As shown in Fig. 7, the reaction process should be described as follows:

Firstly, the high energy hydrogen atoms are produced by electrolysis of water 28, and H₂CO₃ (or HCO₃⁻) is produced from CO₂.

\[
\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^- \quad (8)
\]

Secondly, the H₂CO₃ was reduced by the high energy hydrogen atoms, generated oxalate.

\[
2\text{M-H} + \text{R} \rightarrow \text{M} + \text{R-H} \quad (7)
\]

\[
\text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{H}_2\text{CO}_3 \quad (9)
\]

\[
\text{H}^+ + \text{M} + \text{e}^- \rightarrow \text{M-H} \quad (4)(\text{Volmer})
\]

Thirdly, the H₂C₂O₄ was subsequently reduced by the high energy hydrogen atoms, generated glyoxal. Then the glyoxal reacted with oxalate, involved in the high energy hydrogen atoms) generated oxalate-glycol polymer.

\[
2\text{M-H} + 2\text{H}_2\text{CO}_3 \rightarrow \text{H}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O} + 2\text{M} \quad (10)
\]
Figure 6 | The MS results of the polymer. It is the MS spectrum of the polymer. There are eight fragments that were less than 438 m/z, and the structures of the fragments are arrayed in a table attached in the blank of the picture.

Figure 7 | The proposed reaction pathways of the artificial photosynthesis. It is the proposed reaction pathway of the artificial photosynthesis. Four steps of reactions are included.
4M+ + H₂C₂O₄ → H₂C₂O₃ + 2H₂O + 4M (11)

2nM+ + nH₂C₂O₄ → H₂C₂O₄(ΟH)ₙ + (n-1) H₂O + 2nM (12)

Finally, the oxalate-glycol polymer subsequently was reduced by the high energy hydrogen atoms, generated oxalate-glycol-x-hydroxyl polymer.

Methods

Artificial photosynthesis. 600 ml of 5.0%(W%)NH₄HCO₃ solution were fed into the electronic cell, its anode and cathode plates were constructed using titanium metal electrode and Nickel-chromium-iron alloy electrode (Ni, 14.2%, Cr, 16.7%, Fe, 69.1%), respectively. A 2.5 μm micro porous membrane of polytetrafluoroethylene (PTFE) was used as the separation membrane. A voltage of 5.0 V was obtained from the accumulator, which was charged from a solar panel with its effective area of 0.25 m². The current average 35 mA, the anode plate area was 0.00125 m². Work at atmospheric condition, room temperature (15–28 °C) for 480 hours.

HPLC. The product solution was analyzed by a high performance liquid chromatography, equipped with waters 600 controller and water 2478 dual absorbance detector. The column was a Hypersil C₁₈ 5 μm, the temperature of columns was maintained at 50 ± 1 °C. The eluent was 0.01 mol/L (NH₄)H₂PO₄ solution, and 1.0 mol/L H₂PO₄, PH: 2.7. The flow rate was 1.0 mL/min (11, 12).

GPC. 1.00 mg/ml solution of the neutral solid products was prepared and, and it was determined by a gel permeation chromatography (GPC). A HP/GPC system equipped with Agilent G1362A differential refraction detector, tree columns of Shodex Sugar Elite). The polymer was dissolved in methanol and injected at a flow rate of 3 ml/min. The evidences for existence of glyoxal are tested by Gas Chromatography (GC). A gas chromatograph (Agilent Technologies 6890N) with a polyethylene glycol (GC) range using colour analysis and FTIR spectroscopy. 3. Lin, J., Ding, Z., Hou, Y. & Wang, X. Ionic Liquid Co-catalyzed Artificial Photosynthesis of CO. Sci. Rep. 3, 1056; DOI: 10.1038/srep01056 (2013).

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Author contributions
G.N. involved in the new ideal and design of the device of artificial photosynthesis. S.W. involved in the preparation of the device of artificial photosynthesis. G.N., S.C., Q.Z., H.M. and S.L. involved in separation, determination and analysis of products. Y.X., P.Z. and W.C. involved in the analysis of mass spectrometry. G.N., S.C. and L.H. prepared the manuscript and all authors reviewed the manuscript.

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