Electronic Supplementary Material (ESI) for Communication

Electronic Supplemental Information

For

Conversion of glucose to methyl glycolate in subcritical methanol

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Experimental section

Materials

Anhydrous methanol (GR, 99.9%, with molecular sieves, water content ≤ 50 ppm) and glucose monohydrate were purchased from Tianjin Kermel Reagent Co, China. Analytic methanol (AR, 99.9%) was purchased from Yantai, Shandong, shuangshuang Chemical Reagent Co. (China). Anhydrous glucose (Biotechnology grade 99%) was purchased from Shanghai Macklin Biochemical Technology Co., Ltd. Standard compounds, including methyl glycolate, methyl acetate, dimethyl oxalate, ethylene glycol, ethanol, methyl lactate and glycolaldehyde dimethyl acetal, are purchased from Shanghai Macklin Biochemical Technology Co., Ltd.

Test analysis

All reactions were performed in an autoclave (Anhui Kemi Machinery Technology Co., Ltd.). A mixture of glucose (100 mg) and methanol (10 mL) was placed into a 50 ml stainless steel autoclave. After the autoclave was sealed, the reactor was purged by pure air (1~4 MPa). Then, it was heated to desired temperature (60~240 ℃) and kept for a desired time (1~4 h) at a stirring rate of 600 rpm. The autoclave was quenched in an ice-water mixture after the reaction was over. The obtained solution was collected into a 10 mL bottle for analysis. Standard compounds were applied as references for identification of produces via GC and GC-MS.

Characterization

The Fourier-transform infrared (FT-IR) spectra of the liquid samples were collected on a Bruker Equinox 70 spectrometer (BRUKER) equipped with a mercury cadmium telluride (MCT) detector. In each experiment, approximately 1 mg of the sample was mixed with 100 mg KBr and then pelletized for scanning. UV-vis spectra were analyzed on PerkinElmer Lamda 650S UV-vis spectrometer equipped with a homemade UV-vis cell allowing control of temperature and atmosphere. In a typical test, the sample solution was added into the reaction cell which then flushed with Ar several times. After that, the cell will be loaded in the UV-vis unit for heating treatment. During the process, the UV-vis spectra were collected regularly.

The liquid production was analyzed by the Shimadzu gas chromatography (GC-2030) equipped with a flame ionization detector (FID) via and a capillary column (HP-INNOWAX, 30 m × 0.32 mm × 0.5 μm). Moreover, the external method was used here. Moreover, gas chromatography-mass spectroscopy (GC-MS, Thermo Trace GC Ultra with a Polaris-Q ion trap mass spectrometer) equipped with a HP-INNOWAX capillary column was also applied to qualitative analyze the species in liquid samples. Meanwhile, the total carbon content in the liquid products was measured by a Vario EL elemental analysis (± 0.2%). The yield was calculated as follows.

$$Yield(100\%) = \frac{mass\ of\ carbon\ in\ the\ target\ product}{mass\ of\ carbon\ in\ initial\ glucose} \times 100\%$$
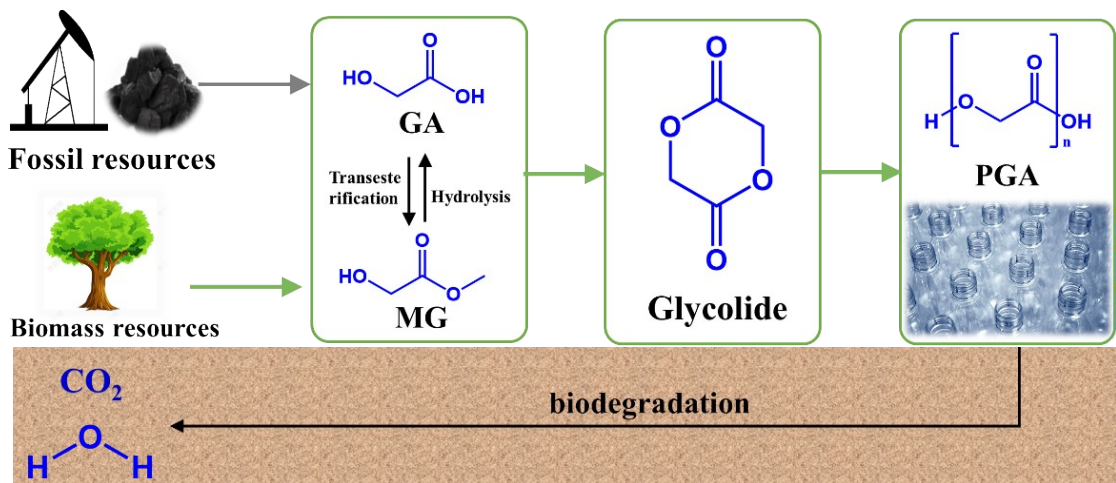
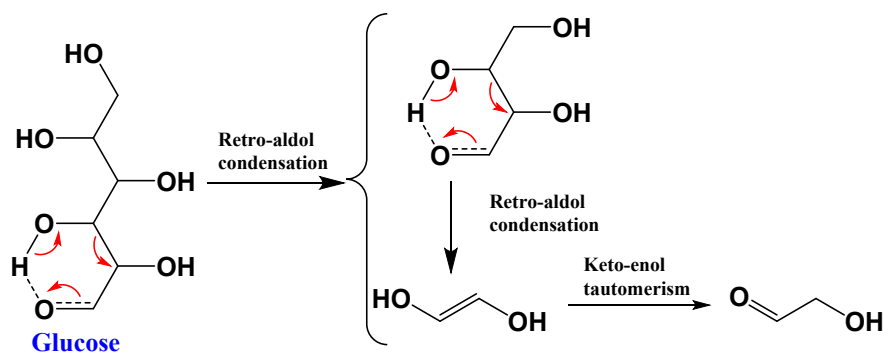**Figure S1**. Currently synthesized methods in the PGA production.

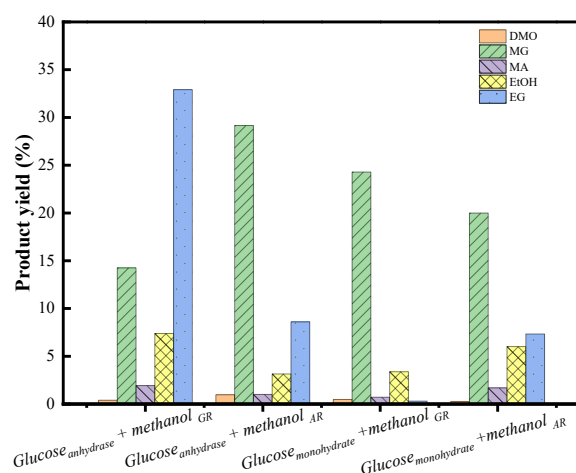**Figure S2**. RAC of sugars in sub-supercritical water without any catalysts[1, 2].

Figure S3. Effect of different substrates and solvent on the glucose conversion, reaction conditions: 0.1 g reactant, 10 mL methanol, 220 °C, 4 h, 4 MPa air.

Water content calculation:

Glucose$_{anhydrous}$ + methanol$_{GR:}$ 50 ppm*10 mL*0.79 g/mL=0.000395 g

Glucose$_{anhydrous}$ + methanol$_{AR:}$ 0.1%*10 mL*0.79 g/mL =0.0079 g

Glucose$_{monohydrate}$ + methanol$_{GR:}$ 0.1 g* (18/198) + 0 ppm*10 mL*0.79 g/mL =0.0095 g

Glucose$_{monohydrate}$ + methanol$_{AR:}$ 0.1 g*(18/198) + 0.1%*10 mL*0.79 g/mL=0.017 g
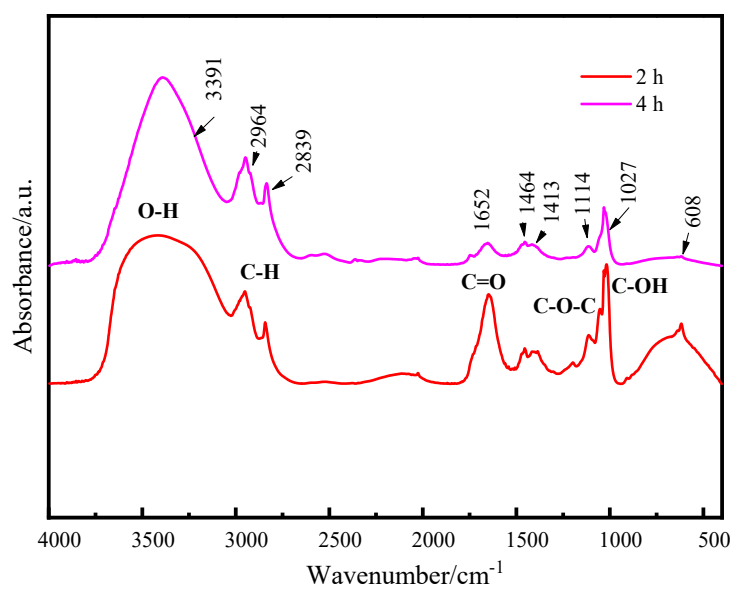
Figure S4. FTIR spectra result of the liquid products at different reaction times.
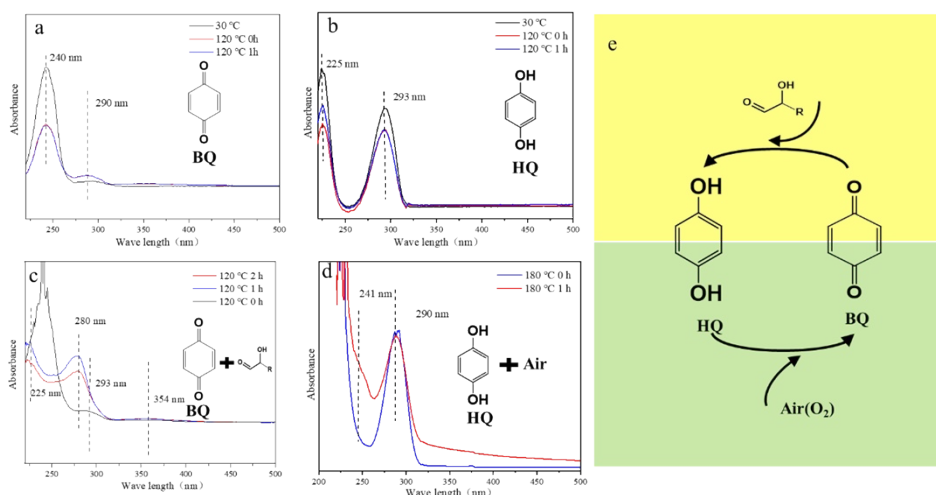
Figure S5. In situ UV/vis analysis of relevant samples: (a) the UV/vis spectra of benzoquinone (BQ) sample in methanol solution under Ar atmosphere during heating process, (b) the UV/vis spectra of hydroquinone (HQ) sample in methanol solution under Ar atmosphere during heating process, (c) the UV/vis spectra of BQ and glucose mixture in methanol solution under Ar atmosphere during heating process, (d) the UV/vis spectra of HQ sample in water solution under O_2 atmosphere during heating process (methanol was replaced with water to prevent it from exploding when oxidized at high temperatures), (e) the possible two half cycles in the phenol/quinone redox system.

To prove the phenol/quinone redox mechanism hypothesis, we conducted *in-situ* UV-vis analysis. Figure 1a (see below) is the UV/vis spectra of benzoquinone (BQ) in methanol solution during heating process, showing characteristic absorption peaks at 240 and 290 nm. Figure 1b is the UV/vis spectra of hydroquinone (HQ), showing characteristic absorption peaks at 225 and 293 nm. As can be seen, BQ and HQ kept a stable absorption band during the heating process. However, when glucose was added into the BQ methanol solution, the absorption band changed significantly with the increase of reaction time during the heating process. As shown in Figure 1c, the original peaks were significantly reduced, with two peaks of around 225 and 280 nm, possibly due to the presence of HQ and glucuronic acid [3, 4]. Other aldoses such as glycolaldehyde and xylose have also been tested in experiments, exhibiting similar behavior. This result indicates that the BQ can react with g aldoses. In addition, the other half cycle of HQ and O_2 were tested. As shown in Figure 1d, the original peaks of HQ slightly reduced, and a new small absorption peak appeared at around 240 nm, which may be attributed to the presence of BQ. From a chemical perspective, HQ can be easily oxidized under O_2 atmosphere. The oxidation in this test is not obvious, possibly because there is less oxygen in the reactor tank and the mixing is not obvious, leading to the limited solubility and reaction in the solution. Clearly, both half cycles in the phenol/quinone redox system can occur independently in the reaction conditions, thus acting as a redox catalytic cycle to drive the conversion of glucose to MG. Thorsten et al. also used 1,4-benzoquinone/1,4-hydroquinone system as a hydrogen reservoir in a photocatalytic water splitting [3]. Xu et al. reported on a similar biomimetic catalytic system driven by

electron transfer form anthraquinone for the selective oxygenation of hydrocarbon [5]. Therefore, the redox catalytic cycle could be chemical applied. As to the catalytic mechanism, it will be further investigated in our future research.

Reference:

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