

RESEARCH

Open Access



# Enhancement of acetate production in hydrogen-mediated microbial electrosynthesis reactors by addition of silica nanoparticles

Zeyan Pan<sup>1</sup>, Zhuangzhuang Liu<sup>1,2</sup>, Xiaona Hu<sup>3</sup>, Kai Cui<sup>1</sup>, Wenfang Cai<sup>1</sup> and Kun Guo<sup>1\*</sup> 

## Abstract

Microbial electrosynthesis (MES) is a promising technology for CO<sub>2</sub> fixation and electrical energy storage. Currently, the low current density of MES limits its practical application. The H<sub>2</sub>-mediated and non-biofilm-driven MES could work under higher current density, but it is difficult to achieve high coulombic efficiency (CE) due to low H<sub>2</sub> solubility and poor mass transfer. Here, we proposed to enhance the hydrogen mass transfer by adding silica nanoparticles to the reactor. At pH 7, 35 °C and 39 A·m<sup>-2</sup> current density, with the addition of 0.3wt% silica nanoparticles, the volumetric mass transfer coefficient ( $k_{La}$ ) of H<sub>2</sub> in the reactor increased by 32.4% (from 0.37 h<sup>-1</sup> to 0.49 h<sup>-1</sup>), thereby increasing the acetate production rate and CE of the reactor by 69.8% and 69.2%, respectively. The titer of acetate in the reactor with silica nanoparticles (18.5 g·L<sup>-1</sup>) was 56.9% higher than that of the reactor without silica nanoparticles (11.8 g·L<sup>-1</sup>). Moreover, the average acetate production rate of the reactor with silica nanoparticles was up to 2.14 g·L<sup>-1</sup>·d<sup>-1</sup> in the stable increment phase, which was much higher than the other reported reactors. These results demonstrated that the addition of silica nanoparticles is an effective approach to enhancing the performance of H<sub>2</sub>-mediated MES reactors.

**Keywords** Microbial electrosynthesis, H<sub>2</sub>-mediated, Silica nanoparticles, Mass transfer, Acetate production

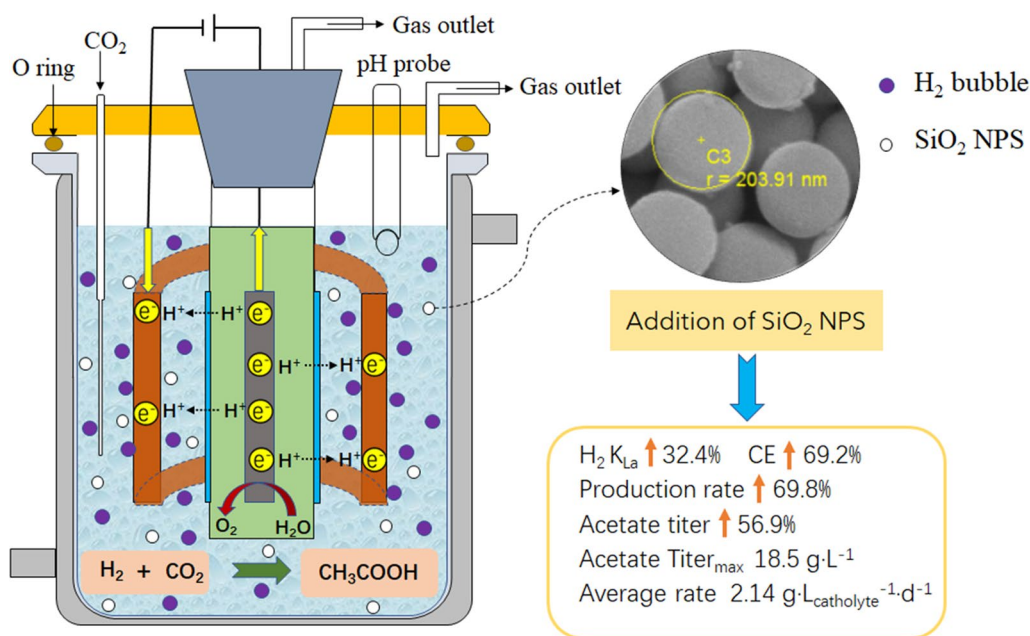
\*Correspondence:

Kun Guo

kun.guo@xjtu.edu.cn

Full list of author information is available at the end of the article

## Graphical Abstract

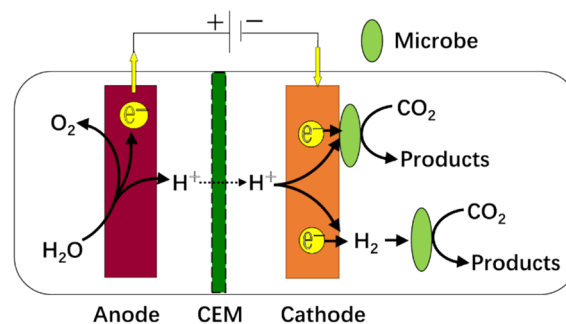


## Introduction

Microbial electrosynthesis (MES) is a process that utilizes microorganisms as the cathodic catalysts for electrochemical  $\text{CO}_2$  reduction (Nevin et al. 2011). Compared to abiotic catalysts, microorganisms have the advantages of high selectivity, self-regenerating ability, and capability of producing multi-carbon organics (Salehizadeh et al. 2020). Consequently, MES has drawn increasing attention in the fields of  $\text{CO}_2$  valorization and renewable energy stargate (Logan & Rabaey 2012). The concept of MES emerged around 2010 after some methanogens (Cheng & Logan 2007) and acetogens were found to be able to uptake electrons from the cathode for the production of methane and acetate, respectively. After that, a lot of work has been done to modify electrode materials, discover effective microorganisms, understand extracellular electron transfer (EET) mechanisms, and develop novel reactor configurations (Aryal et al. 2017; Krieg et al. 2014). The current density (i.e., productivity) of MES has improved a lot, but it is too low to bring this technology onto the market (Jourdin & Burdyny 2021; Prevot et al. 2020).

Figure 1 shows the working principle of MES. In this system, renewable electricity is used to oxidize  $\text{H}_2\text{O}$  to form  $\text{O}_2$ ,  $\text{H}^+$ , and  $\text{e}^-$  in the anodic chamber, and then  $\text{H}^+$  and  $\text{e}^-$  are transported to the cathode chamber in which they are used by autotrophic microbes to fix

$\text{CO}_2$  for organic matter production. The conventional MES was driven by the biofilm on the cathode surface, because biofilm enabled high coulombic efficiency (CE), low energy input, and good biomass retention (Fruehauf et al. 2020). However, the current density of the biofilm-driven MES was limited by the activity of the biomass and the mass transfer efficiency. Currently, the current density of cathodic biofilms has reached the maximum values of electro-active biofilms (i.e.,  $10\text{--}100 \text{ A}\cdot\text{m}^{-2}$ ) (Claassens et al. 2019). Thus, it is very challenging to further increase the current density of biofilm-driven MES, especially for its large-scale applications. Therefore, non-biofilm-driven MES has been proposed recently. This non-biofilm-driven MES used suspended biomass and



**Fig. 1** The schematic of MES reactors (CEM: cation exchange membrane)

hydrogen produced from the cathode for CO<sub>2</sub> conversion, which was also named H<sub>2</sub>-mediated MES. Without the limitation of biofilm, high current density could be applied to the reactor for hydrogen production. However, the low solubility and poor mass transfer of H<sub>2</sub> make it difficult to achieve high CE under high current density for this type of H<sub>2</sub>-mediated MES (Liu et al. 2016).

Previously, it has been reported that the enhancement of H<sub>2</sub> mass transfer is an effective method to improve the performance of H<sub>2</sub>-mediated MES reactors. For example, Rodrigues et al. reported that adding perfluorocarbon nanoemulsion (a hydrogen carrier) into H<sub>2</sub>-mediated MES increased the productivity of acetate by 190% and obtained a CE of nearly 100% (Rodrigues et al. 2019). Our group also found that adding porous polyurethane (PPU) particles could promote the hydrogen uptake efficiency and acetate production rate in an H<sub>2</sub>-mediated MES reactor (Xue et al. 2022). Moreover, nanoparticles have also been applied to syngas fermentation and methane fermentation to improve the gas–liquid mass transfer (Kim et al. 2014; Zhu et al. 2008). Therefore, we hypothesized that introducing nanoparticles to H<sub>2</sub>-mediated MES may also enhance the hydrogen mass transfer, CE and acetate production rate. Among all reported nanoparticles, silica nanoparticles (SiO<sub>2</sub> NPS) are biocompatible, dispersible in water, and commercially available at a relatively cheap price. Compared to perfluorocarbon nanoemulsion, SiO<sub>2</sub> NPS can be easily separated from the fermentation broth for reuse. The PPU particles are on a millimeter scale, so that they can be easily maintained in the reactor, but the specific surface area of PPU is rather limited when compared to SiO<sub>2</sub> NPS. Adding SiO<sub>2</sub> NPS may further improve the hydrogen mass transfer in H<sub>2</sub>-mediated reactors. Thus, the goal of this study was to investigate whether the addition of SiO<sub>2</sub> NPS could enhance the hydrogen mass transfer and the performance of an H<sub>2</sub>-mediated MES.

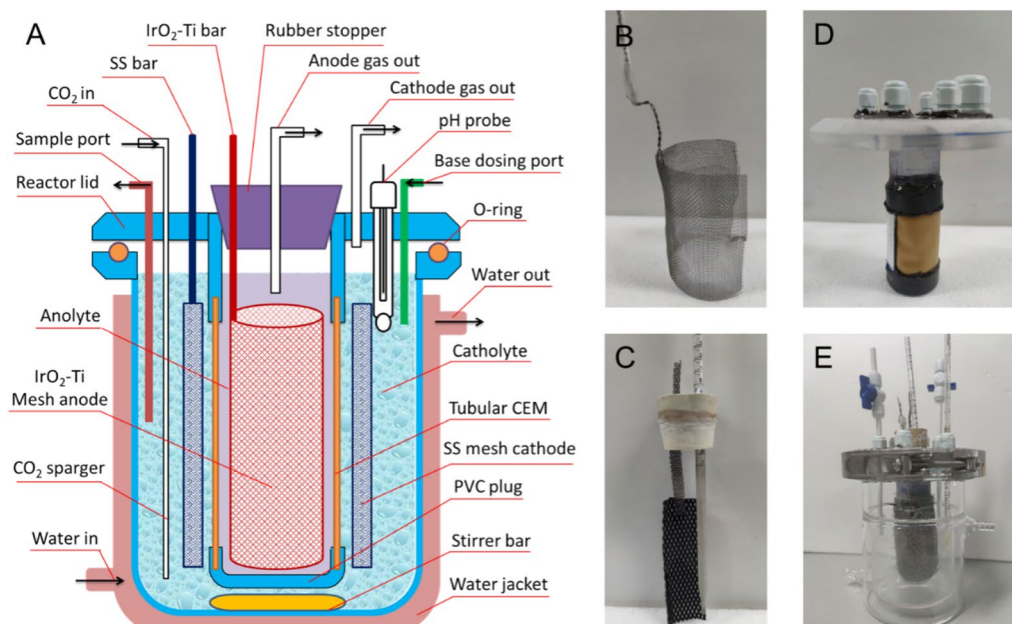
Our experimental results showed that the addition of SiO<sub>2</sub> NPS in the MES system could significantly increase the H<sub>2</sub> mass transfer rate and H<sub>2</sub> solubility in water, thereby increasing the acetate production rate by 69.8% and the acetate titer by 56.9%. The average acetate production rate of the reactor with silica nanoparticles (2.14 g·L<sup>-1</sup>·d<sup>-1</sup>) was higher than those of the reported MES reactors. These results demonstrated adding SiO<sub>2</sub> NPS is an efficient way to enhance the performance of H<sub>2</sub>-mediated MES reactors. The method reported here dramatically increases the current density and coulombic efficiency of H<sub>2</sub>-mediated MES reactors. It can not only be applied in H<sub>2</sub>-mediated MES reactors for acetate and methane production but also in other H<sub>2</sub>-dependent reactions, such as biologically catalyzed N<sub>2</sub> fixation, CH<sub>4</sub> functionalization and microbial protein production.

## Materials and methods

### Reactor design and construction

An electrochemical continuous stirred-tank reactor (E-CSTR) was used for this study. The design of the E-CSTR is shown in Fig. 2. The reactor consisted of a tubular anode membrane assembly and a jacketed mixing vessel (outer diameter: 12.4 cm, inner diameter: 10.7 cm, height: 14.5 cm, maximum volume: 1 L). The anode membrane assembly consisted of a lid and a tubular membrane cell (diameter: 3.5 cm, height: 12.5 cm) that was placed in the middle of the lid. The bottom of the anode chamber was sealed by a PVC cap, while the top was plugged with a rubber stopper. The rubber stopper held the anode and an anode gas outlet tube. The size of the cation exchange membrane (CMI-7000, Membranes International Inc., USA) window on the anode membrane assembly was 42 cm<sup>2</sup> (6 cm × 7 cm). There were six openings on the lid of the reactor, and they were used for the Stainless steel bar cathode current collector, CO<sub>2</sub> inlet tube, base dosing tube, pH probe, cathode gas outlet tube, and liquid sample port. A stainless-steel mesh cylinder (length: 16 cm, height: 8 cm, thickness: 0.3 mm, Anguo Chengli Metal Co., Ltd., China) was used as the cathode. An IrO<sub>2</sub>-coated titanium mesh plate (width: 3.2 cm, height: 8 cm, Baoji Zhiming Special Metal Co., Ltd., China) was used as the anode. The reactor lid and the flange of the mixing vessel were sealed by an O-ring and a clamp.

The working volume of the anolyte and catholyte was 100 mL and 600 mL, respectively. The anolyte was 0.2 mol·L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> solution, and its pH was adjusted to 2 with H<sub>2</sub>SO<sub>4</sub>. The catholyte was a modified M9 medium containing 6 g·L<sup>-1</sup> Na<sub>2</sub>HPO<sub>4</sub>, 3 g·L<sup>-1</sup> KH<sub>2</sub>PO<sub>4</sub>, 0.5 g·L<sup>-1</sup> NH<sub>4</sub>Cl, 0.5 g·L<sup>-1</sup> NaCl, 0.1 g·L<sup>-1</sup> MgSO<sub>4</sub>·7H<sub>2</sub>O, 0.0146 g·L<sup>-1</sup> CaCl<sub>2</sub>, 4 g·L<sup>-1</sup> NaHCO<sub>3</sub>, 1 mL·L<sup>-1</sup> trace element solution and 1 mL·L<sup>-1</sup> vitamin solution. The compositions of the trace element solution and vitamin solution were provided in Table S1. The jacketed mixing vessel was connected to a recirculating water bath (DC-1006, Ningbo Scientz Biotechnology Co., Ltd., China) to control the reactor temperature. A magnetic stirrer was placed at the bottom of the vessel to control the agitation intensity of the catholyte. The anode and cathode were connected to the positive and negative terminals of the DC power supply (KA3005P, Korad Technology Co., Ltd., China), respectively. The pH of the catholyte was controlled with a pH controller (pH3.0-NI2-AC, Huzhou Tianze Biotechnology Co., Ltd., China) by automatically dosing 5 M NaOH. The reactor was equipped with a mass flow controller (D07-7, Beijing Sevenstar Flow Co., Ltd, China) to control the CO<sub>2</sub> flow rate. A water displacement column (filled with 1200 mL 1 mM HCl) was



**Fig. 2** The schematic of the E-CSTR reactor (A) and photos of the reactor parts (B: the cathode; C: the anode; D: the anode membrane assembly; E: the jacketed mixing vessel)

connected to the reactor to collect the offgas for gas flow rate and composition measurement.

### Reactor startup and operational procedure

Two reactors were run in parallel, one as the control and the other one as the experimental reactor. The SiO<sub>2</sub> NPS used in this study were commercial hydrophilic SiO<sub>2</sub> NPS that was produced by the sol-gel method (average diameter 200 nm, Hebei Juli Metal Material Co., Ltd., China). The SiO<sub>2</sub> NPS could easily disperse in water so they were used as purchased without any pretreatment.

In the control reactor, no SiO<sub>2</sub> NPS were added, while in the experimental reactor 0.3wt% SiO<sub>2</sub> NPS were added (1.8 g of SiO<sub>2</sub> NPS were added into 600 mL of catholyte). The dosage of the SiO<sub>2</sub> NPS (0.3wt%) was chosen based on literature regarding syngas fermentation enhancement by adding SiO<sub>2</sub> NPS (Kim et al. 2014).

The reactor temperature was controlled at  $35 \pm 0.5$  °C by the water bath, and the stirring rate of the magnetic stirrer was set at 650 rpm. The catholyte of the reactor was first flushed with N<sub>2</sub> for 30 min to remove the dissolved oxygen. Then, the cathode chamber was inoculated with an enriched acetate-producing mixed culture that was dominated by *Acetobacterium*. The reactor was operated in a galvanostatic mode with a starting current of 0.25 A and then switched to 0.5 A. At 0.25 and 0.5A, the CO<sub>2</sub> flow rate was controlled at 1.96 and 3.92 mL·min<sup>-1</sup>, respectively, which resulted in an H<sub>2</sub>/

CO<sub>2</sub> molar ratio of 2:1. The pH of the catholyte was controlled at 7 using the pH controller.

Each day, 2 mL of catholyte was taken to measure the pH and VFAs, and the same amount of fresh catholyte was added. Occasionally, fresh anolyte was added to the anode chamber to compensate for the water loss. The reactors were operated in fed-batch mode. When the acetate concentration stopped increasing, 90% of the catholyte was replaced with a fresh medium to start a new batch. In the second batch, 0.3wt% SiO<sub>2</sub> NPS were added to the experimental reactor.

### Analytical methods

#### Gas analysis

Gas samples were taken from the water displacement column to analyze the volume and composition of the unused gas. The gas composition, i.e., the concentrations of H<sub>2</sub> and CO<sub>2</sub>, was analyzed by a compact gas chromatograph (GC, 7890B, Agilent). Details of the method could be found in our previous publication (Cai et al. 2022).

#### VFAs analysis

Liquid samples were taken from the reactor to analyze the concentration of acetate. The liquid samples were first extracted by diethyl ether and then injected into gas chromatography (GC-2010 Pro, AOC-201, Shimadzu, Japan) with an FID detector to analyze. Details of these



methods could be found in our previous publication (Cai et al. 2022).

#### Hydrogen mass transfer coefficient measurement

The volumetric mass transfer coefficient ( $K_{La}$ ,  $\text{h}^{-1}$ ) which describes the transfer resistance at the gas–liquid interface was tested by the dynamic-gasing method described in a previous article (Beckers et al. 2015). Briefly, the reactor was filled with M9 medium without inoculum. The temperature was kept at 35 °C. The reactor was equipped with a dissolved hydrogen sensor (Clean, DH200, China) at the cover to measure and record dissolved  $\text{H}_2$  concentrations. The  $K_{La}$  of  $\text{H}_2$  in the reactor with  $\text{SiO}_2$  NPS and that without  $\text{SiO}_2$  NPS were measured under 0.5 A in abiotic conditions. For each experiment, the reactor was degassed with  $\text{N}_2$  to remove  $\text{H}_2$  before electrolysis. The values of the dissolved hydrogen sensor were recorded once a minute until reaching saturation.

#### Calculations

The  $k_{La}$  was calculated according to the adsorbing equation (Myung et al. 2016):

$$\frac{dC}{dt} = K_L a (C^* - C) \quad (1)$$

Here,  $C^*$  is the saturated concentration of dissolved hydrogen ( $\text{mg H}_2 \text{ L}^{-1}$ ),  $K_L$  is the mass transfer coefficient ( $\text{cm} \cdot \text{h}^{-1}$ ), and  $a$  is the gas/liquid interfacial area per volume of liquid ( $\text{cm}^2 \cdot \text{cm}^{-3}$ ).

The CE was calculated as described earlier (Liu et al. 2015), to reflect the productivity of the system:

$$CE = \frac{\Delta C_{\text{HAc}} (\text{mol L}^{-1}) \times V_{\text{solution}} (\text{L}) \times 8 \times F (\text{C mol}^{-1})}{\text{Overall charge (C)}} \times 100\% \quad (2)$$

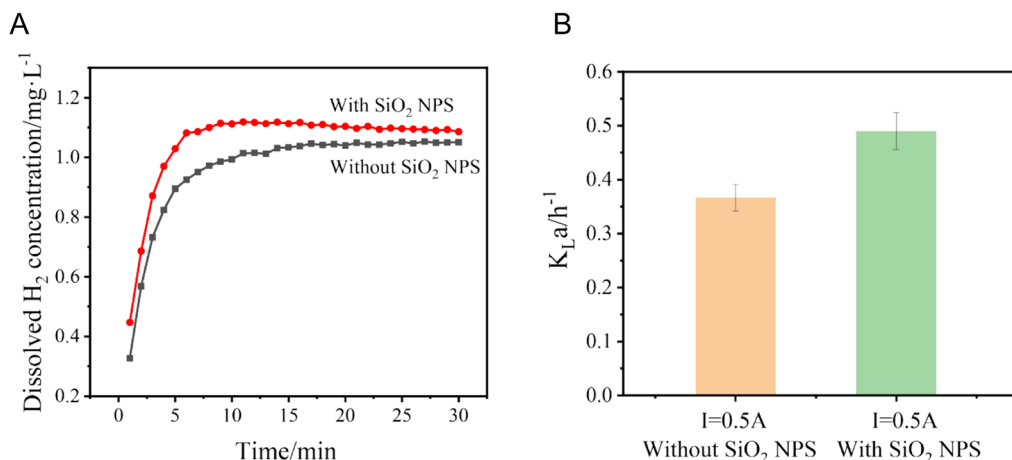
Here,  $\Delta C_{\text{HAc}}$  ( $\text{mol} \cdot \text{L}^{-1}$ ) is the change in the concentration of acetate during the experiment,  $V_{\text{solution}}$  is the total volume of the solution in the cathode chamber, and ‘Overall charge’ is the total electric charge passing through the cathode chamber and  $F$  is the Faraday’s constant.

## Results and discussion

### $k_{La}$ determination and dissolved $\text{H}_2$ concentration

The  $K_{La}$  was measured under different conditions to determine the mass transfer rate of dissolved  $\text{H}_2$  at the gas–liquid interface (Fig. 3B). At 0.5 A, the  $K_{La}$  of the reactor added with  $\text{SiO}_2$  NPS reached  $0.49 \text{ h}^{-1}$ , which was 32.4% higher than that reached without  $\text{SiO}_2$  NPS ( $0.37 \text{ h}^{-1}$ ). The relation between the dissolved  $\text{H}_2$  concentration and the electrolysis time is shown in Fig. 3A. With the addition of  $\text{SiO}_2$  NPS, the saturated dissolved  $\text{H}_2$  concentration increased from  $1.04 \text{ mg} \cdot \text{L}^{-1}$  to  $1.11 \text{ mg} \cdot \text{L}^{-1}$  at 0.5 A. All these results confirmed that adding  $\text{SiO}_2$  NPS to the catholyte could improve the mass transfer of the dissolved  $\text{H}_2$  in the gas–liquid interface and increase the saturated dissolved  $\text{H}_2$  concentration of the reactor.

The kinetics of  $\text{H}_2$  oxidation by hydrogenase is rate-dependent for  $\text{H}_2$ -induced  $\text{CO}_2$  reduction. As  $\text{H}_2$  has a limited solubility of 0.79 mM (Liu et al. 2016) in water at ambient conditions. Based on the information obtained from our experiments, the  $\text{H}_2$   $K_{La}$  of the reactors could be increased by introducing  $\text{SiO}_2$  NPS. The improvement of the mass transfer coefficient by the interaction between nanoparticles and the gas–liquid interface could be



**Fig. 3** The dissolved  $\text{H}_2$  concentration curves (A) and the  $K_{La}$  of  $\text{H}_2$  (B) of reactors at 0.5 A under abiotic conditions

explained by three theories: a shuttling or grazing effect, hydrodynamic influences at the gas–liquid interface, and changes in the specific gas–liquid interfacial area (Kim et al. 2014). The diameter of the nanoparticles was much smaller than that of the gas–liquid boundary layer, which is usually 5–25  $\mu\text{m}$ . Therefore, it was likely that shuttling or grazing effects played an important role in improving gas–liquid mass transfer (Kim et al. 2014).

### Acetate production

As shown in Fig. 4B, the acetate production rate was lower than  $0.50 \text{ g}\cdot\text{L}^{-1}\cdot\text{d}^{-1}$  in the first 2 days, but it increased sharply in the coming days. When  $\text{SiO}_2$  NPS were present in the reactor, the acetate concentration increased from  $0.29 \text{ g}\cdot\text{L}^{-1}$  to  $13.1 \text{ g}\cdot\text{L}^{-1}$  (2–8 days), and the average acetate production rate reached  $2.14 \text{ g}\cdot\text{L}^{-1}\cdot\text{d}^{-1}$  in batch 1. In contrast, the acetate production rate and the final acetate concentration of the experiment without  $\text{SiO}_2$  NPS were only  $1.16 \text{ g}\cdot\text{L}^{-1}\cdot\text{d}^{-1}$  and  $7.22 \text{ g}\cdot\text{L}^{-1}$  in batch 1, respectively. The second batch displayed a comparable production profile, but the acetate titer outperformed the first batch. The maximum acetate concentration and average acetate production rate (10–18 days) of the experiments in batch 2 with (without) particles were  $18.5$  ( $11.8$ )  $\text{g}\cdot\text{L}^{-1}$  and  $2.14$  ( $1.26$ )  $\text{g}\cdot\text{L}^{-1}\cdot\text{d}^{-1}$ , respectively.

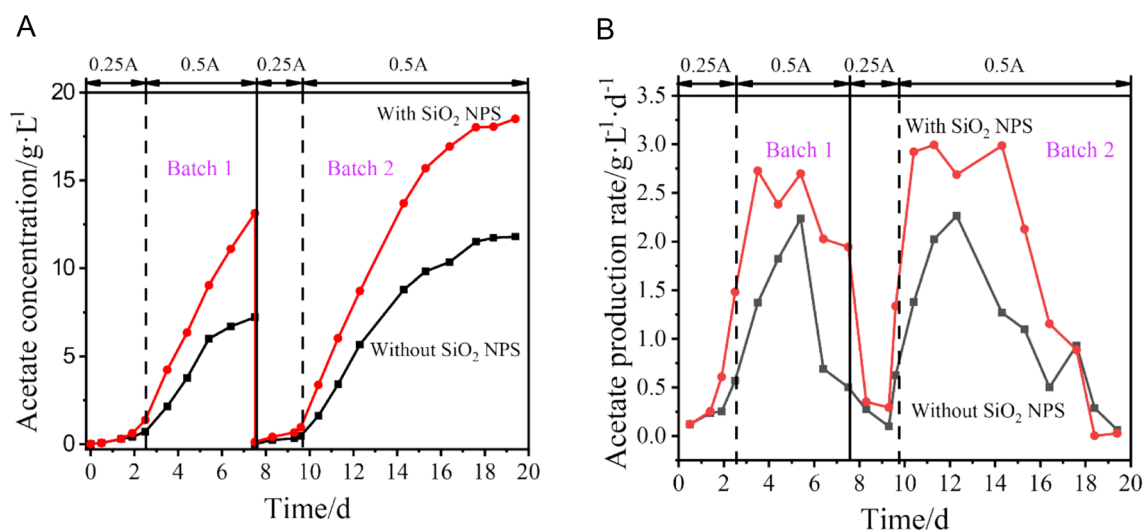
The performance of the second batch was superior to the first batch in terms of acetate titer due to the enrichment of more acetate-tolerating microorganisms during the long-term operation. In batch 2, the acetate production rate with nanoparticles was 1.7 times higher than that without nanoparticles at the stable increment stage (10–18 days) of acetate, and the titer of acetate increased

by 56.9%. All these results suggested that the addition of  $\text{SiO}_2$  NPS could improve both the acetate production rate and titer of acetate by enhancing the mass transfer of the dissolved  $\text{H}_2$  at the gas–liquid interface and increasing the saturated dissolved  $\text{H}_2$  concentration in the reactor. This could be attributed to the fact that enhanced gas–liquid mass transfer would normally increase the amount of biomass in the reactor (Xue et al. 2022).

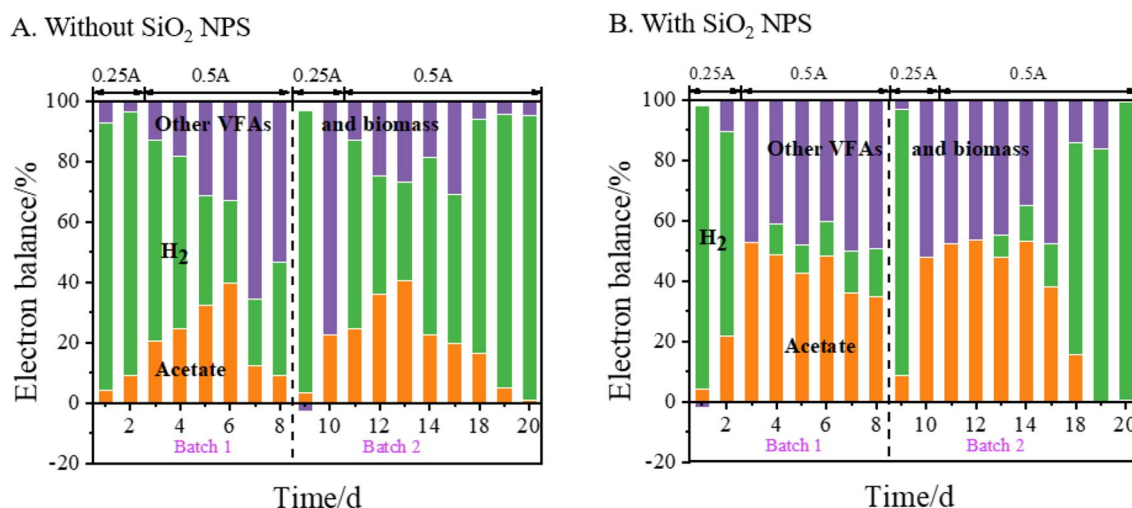
### Electron balance

Based on the VFAs concentration and the  $\text{H}_2$  left in the reactor, the electron balance was calculated. Most of the electrons from the cathode ended up in acetate and  $\text{H}_2$ , while the rest could be attributed to other VFAs and biomass (Fig. 5). In general, the percentage of electrons that went to acetate increased at first and then decreased over time, whereas the percentage of electrons that ended in  $\text{H}_2$  decreased at first and then increased over time. In batch 1, the average percentages of electrons that went to the acetate of the reactor with and without  $\text{SiO}_2$  NPS were 36% and 19%, respectively. In the stable increment phase (10–18 days) of batch 2, the average percentage of electrons went to acetate, other VFAs and biomass, and  $\text{H}_2$  were 44%, 41%, and 15% with  $\text{SiO}_2$  NPS, while those without  $\text{SiO}_2$  NPS were 26%, 28%, and 46%, respectively. Therefore, the addition of  $\text{SiO}_2$  NPS could make more electrons go to acetate instead of  $\text{H}_2$ .

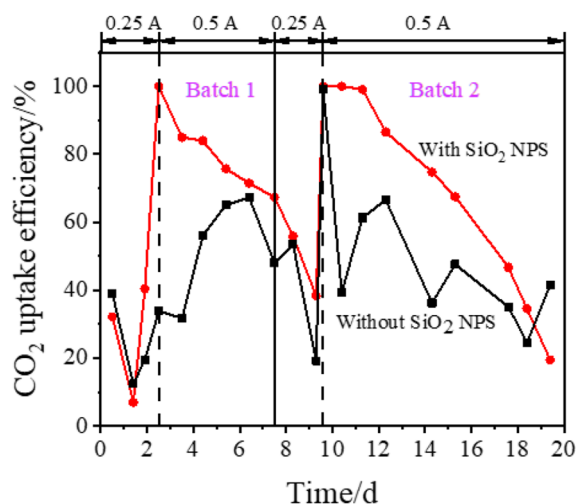
In the stable increment phase, the reactor without  $\text{SiO}_2$  NPS reached its throughput bottleneck, because 50% of the electrical  $\text{H}_2$  was not utilized by the culture due to the limitation of  $\text{H}_2$  solubility in water. In contrast, the addition of  $\text{SiO}_2$  NPS can alleviate the throughput bottleneck



**Fig. 4** The acetate concentration (A) and acetate production rate (B) of the MES reactor in two batches



**Fig. 5** The electron balance of the MES reactor in two batches



**Fig. 6** CO<sub>2</sub> uptake efficiency of the MES reactor in two batches. At 0.25 A and 0.5 A, the CO<sub>2</sub> flow rates were 1.96 mL·min<sup>-1</sup> and 3.92 mL·min<sup>-1</sup>, respectively

by reducing the limitation and making almost all H<sub>2</sub> be utilized by the culture.

#### CO<sub>2</sub> uptake efficiency

The CO<sub>2</sub> uptake efficiency (Fig. 6) was consistent with electron balance. To facilitate the acclimation of the microbial community, the reactor was operated under 0.25 A in the first two days. And the CO<sub>2</sub> uptake efficiency of the reactor with SiO<sub>2</sub> NPS reached 100%. Then, the applied current and the flow rate of CO<sub>2</sub> were doubled. As shown in Fig. 6, the CO<sub>2</sub> uptake efficiency with SiO<sub>2</sub> NPS was over 60% except for some slight fluctuations, while the CO<sub>2</sub> uptake efficiency without SiO<sub>2</sub>

NPS was between 30% and 70%. After that, the rapidly decreased CO<sub>2</sub> uptake efficiency might be caused by product inhibition during the last two days of each batch. All these results indicated that the addition of SiO<sub>2</sub> NPS could increase the CO<sub>2</sub> uptake efficiency of the reactor.

In a broader context, SiO<sub>2</sub> NPS may improve gas solubilities in water for a series of small non-polar gases, such as N<sub>2</sub> and CH<sub>4</sub>, whose solubilities in an aqueous medium are also rate-limiting. We propose that SiO<sub>2</sub> NPS are also potentially applicable for biologically catalyzed N<sub>2</sub> fixation and CH<sub>4</sub> functionalization (Rodrigues et al. 2019), two challenging processes in small molecule activation.

#### Comparison to other MES reactors

The performance of this H<sub>2</sub>-mediated MES reactor was compared to other reported MES reactors in Table 1. Most studies were devoted to improving biofilm formation by developing effective cathodes. Apparently, the current density and acetate production rate of 3D porous cathodes were much higher than those of 2D cathodes in most reported MES reactors. It was simply because the 3D porous cathode could provide a higher specific surface area for the microorganisms and formed a thicker biofilm on the electrode. To our best knowledge, the acetate production rate of all reported MES reactors was less than 1.06 g·L<sup>-1</sup>·d<sup>-1</sup>, and the maximum acetate concentration was around 10 g·L<sup>-1</sup>. By contrast, the acetate production rate and acetate titer of this reactor containing SiO<sub>2</sub> NPS could reach 2.14 g·L<sup>-1</sup>·d<sup>-1</sup> and 18.5 g·L<sup>-1</sup>, respectively, which were about twice those of the reported reactors.

These results could be partly attributed to the better mass transfer to suspended cells in the reactor. Compared to biofilm, the suspended cells had lower limitations

**Table 1** Performance of most acetate-producing MES ( $Q_{\text{Surface}}$ : Surface production rate;  $Q_{\text{Volumetric}}$ : Volumetric production rate.)

Cathode material	Inoculum	$V_{\text{catholyte}}$ (L)	$J$ ( $\text{A}\cdot\text{m}^{-2}$ )	$Q_{\text{Surface}}$ ( $\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ )	$Q_{\text{Volumetric}}$ ( $\text{g}\cdot\text{L}^{-1}\cdot\text{d}^{-1}$ )	Titer ( $\text{g}\cdot\text{L}^{-1}$ )	CE (%)	Refs
Chitosan-coated carbon cloth	<i>Sporomusa ovata</i>	0.2	0.47	13.51	0.317	0.59	86	Zhang et al. 2013
Pr0.5BSCF-CF	Mixed culture	–	– 5.6	96	0.24	7.31	73	Tian et al. 2020
CF with fluidized GAC	Mixed culture	0.28	– 4	–	0.14	3.9	65	Dong et al. 2018
$\text{Mo}_2\text{C}$ -CF	Mixed culture	0.28	– 15	87.5	0.15	4.5	55	Huang et al. 2020
Graphite granules	Mixed culture	0.075	–	–	1.04	10.5	69	Marshall et al. 2013
rGO-CF	Mixed culture	0.28	– 4.9	68	0.17	7.1	77	Song et al. 2017
CNTs–RVC	Mixed culture	0.25	37	195	0.03	1.65	78	Jourdin et al. 2014
CF	Mixed culture	0.25	– 5	19	0.06	1.29	58	Patil et al. 2015
Carbon felt	Mixed culture	0.35	5	20.4	0.58	13.5	61	Gildemyn et al. 2015
VITO–CoRE	Mixed culture	0.5	0.069	46.7	0.14	4.97	45.5	Mohanakrishna et al. 2018
Graphene-carbon felt	<i>Sporomusa ovata</i>	0.25	– 0.23	62.4	0.124	1.88	83	Aryal et al. 2016
CNTs-coated Porous Ni hollow fiber	<i>Sporomusa ovata</i>	0.125	0.332	14.82	0.172	0.084	83	Bian et al. 2018
Carbon felt	Mixed culture	0.2	5	11.5	1.06	5.7	63	Arends et al. 2017
SS	Mixed culture	0.6	39	102	2.14	18.5	44	This work

caused by the substrate and product diffusion and electrode surface area, which could significantly improve the production rate of the bacteria. Furthermore, the addition of  $\text{SiO}_2$  NPS further increased the mass transfer rate of dissolved  $\text{H}_2$ . However, nanoparticles could aggregate and gravitationally settle down in the stagnant flow region (dead zone) in the reactor. Moreover, the behavior of nanoparticles penetrating the cell cytoplasm may be toxic to the cell (Hwang et al. 2008). To obtain the best performance of acetate production, the optimum type and concentration of nanoparticles need to be further studied. In addition, many strategies, such as developing 3D structures and modifying functional groups on the surface of the nanoparticle could be utilized to increase the mass transfer rate and recyclability of nanoparticles. In the future, we could centrifuge the effluent to test whether it is possible to recover the silica nanoparticles for reuse, and we could also modify the silica nanoparticles into magnetic silica nanoparticles to reuse them.

## Conclusion

In summary, this work developed a novel strategy, i.e., adding  $\text{SiO}_2$  NPS, to improve the  $\text{H}_2$  solubility in the  $\text{H}_2$ -mediated MES reactor. We found that the addition of  $\text{SiO}_2$  NPS in the MES system could significantly increase the  $\text{H}_2$  mass transfer rate and maximum saturated  $\text{H}_2$  solubility in water to accelerate the production rate and titer of acetate. With the addition of 0.3wt%  $\text{SiO}_2$  NPS, the  $\text{H}_2$   $K_{\text{La}}$  of the reactor increased by 32.4% at 0.5 A. The titer of acetate in batch 2 of the reactor with  $\text{SiO}_2$  NPS

( $18.5 \text{ g}\cdot\text{L}^{-1}$ ) was 56.9% higher than the reactor without  $\text{SiO}_2$  NPS ( $11.8 \text{ g}\cdot\text{L}^{-1}$ ). In the stable increment phase, the average acetate production rate of the reactor with  $\text{SiO}_2$  NPS reached  $2.14 \text{ g}\cdot\text{L}^{-1}\cdot\text{d}^{-1}$ , which was much higher than other reports. This pioneering effort made with the addition of  $\text{SiO}_2$  NPS provided insights for the development of effective microbial electrosynthesis applications. In a broader context, the nanoparticle can also be utilized in other  $\text{H}_2$ -dependent reactions, such as biologically catalyzed  $\text{N}_2$  fixation,  $\text{CH}_4$  functionalization and microbial protein production.

## Abbreviations

MES	Microbial electrosynthesis
CEM	Cation exchange membrane
CE	Coulombic efficiency
$K_{\text{La}}$	Volumetric mass transfer coefficient
EET	Extracellular electron transfer
$\text{SiO}_2$ NPS	Silica nanoparticles
PPU	Porous polyurethane
E-CSTR	Electrochemical continuous stirred-tank reactor

## Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s40643-023-00627-6>.

**Additional file 1: Figure S1.** SEM of the  $\text{SiO}_2$  NPS. **Figure S2.** Dissolved  $\text{H}_2$  concentration curves (A) and  $K_{\text{La}}$  of  $\text{H}_2$  (B) of reactors at 0.25 A. **Figure S3.**  $\text{H}_2$  uptake efficiency (A) and CE (B) of the MES reactor in two batches. **Table S1.** Composition of trace element solution and vitamin solution.

## Acknowledgements

Not applicable.



## Author contributions

ZP: conceptualization, visualization, writing and editing, experiment. ZL: writing and editing and validation. XH: writing and editing and validation. KC: editing. WC: supervision, validation, conceptualization, writing and editing. All authors read and approved the final manuscript.

## Funding

This work was sponsored by the National Natural Science Foundation of China (No. 22008194), the Natural Science of Shaanxi (No.2020JM-042, No. 2021JQ-012, and No. 2022JQ-087), China Postdoctoral Science Foundation (No.2020M673414, and No. 2020M683502).

## Availability of data and materials

All data generated or analyzed during this study are included in this article.

## Declarations

### Ethics approval and consent to participate

Not applicable.

### Consent for publication

Not applicable.

### Competing interests

The authors declare that they have no competing interests.

### Author details

<sup>1</sup>School of Chemical Engineering and Technology, Xi'an Jiaotong University, Xi'an 710049, China. <sup>2</sup>College of Veterinary Medicine, Northwest A&F University, Yangling 712100, China. <sup>3</sup>School of Ecology and Environment, Zhengzhou University, Zhengzhou 450001, China.

Received: 27 October 2022 Accepted: 9 January 2023

Published online: 20 January 2023

## References

- Arends JBA, Patil SA, Roume H, Rabaey K (2017) Continuous long-term electricity-driven bioproduction of carboxylates and isopropanol from CO<sub>2</sub> with a mixed microbial community. *J CO<sub>2</sub> Util* 20:141–149
- Aryal N, Halder A, Tremblay P-L, Chi Q, Zhang T (2016) Enhanced microbial electrosynthesis with three-dimensional graphene functionalized cathodes fabricated via solvothermal synthesis. *Electrochim Acta* 217:117–122
- Aryal N, Ammam F, Patil SA, Pant D (2017) An overview of cathode materials for microbial electrosynthesis of chemicals from carbon dioxide. *Green Chem* 19(24):5748–5760
- Beckers L, Masset J, Hamilton C, Delvigne F, Toye D, Crine M, Thonart P, Hilgmann S (2015) Investigation of the links between mass transfer conditions, dissolved hydrogen concentration and biohydrogen production by the pure strain *Clostridium butyricum* CWB11009. *Biochem Eng J* 98:18–28
- Bian B, Alqahtani MF, Katuri KP, Liu D, Bajracharya S, Lai Z, Rabaey K, Saikaly PE (2018) Porous nickel hollow fiber cathodes coated with CNTs for efficient microbial electrosynthesis of acetate from CO<sub>2</sub> using *Sporomusa ovata*. *J Mater Chem A* 6(35):17201–17211
- Cai W, Cui K, Liu Z, Jin X, Chen Q, Guo K, Wang Y (2022) An electrolytic-hydrogen-fed moving bed biofilm reactor for efficient microbial electrosynthesis of methane from CO<sub>2</sub>. *Chem Eng J* 132093
- Cheng S, Logan BE (2007) Sustainable and efficient biohydrogen production via electrohydrogenesis. *P Natl Acad Sci USA* 104(47):18871–18873
- Claessens NJ, Cotton CAR, Kopjar D, Bar-Even A (2019) Making quantitative sense of electromicrobial production. *Nat Catal* 2(5):437–447
- Dong Z, Wang H, Tian S, Yang Y, Yuan H, Huang Q, Song TS, Xie J (2018) Fluidized granular activated carbon electrode for efficient microbial electrosynthesis of acetate from carbon dioxide. *Bioresour Technol* 269:203–209
- Fruehauf HM, Enzmann F, Harnisch F, Ulber R, Holtmann D (2020) Microbial electrosynthesis-an inventory on technology readiness level and performance of different process variants. *Biotechnol J* 15(10):e2000066
- Gildemyn S, Verbeeck K, Slabbinck R, Andersen SJ, Prévosteau A, Rabaey K (2015) Integrated production, extraction, and concentration of acetic acid from CO<sub>2</sub> through microbial electrosynthesis. *Environ Sci Technol Lett* 2(11):325–328
- Huang H, Huang Q, Song TS, Xie J (2020) In situ growth of Mo<sub>2</sub>C on cathodes for efficient microbial electrosynthesis of acetate from CO<sub>2</sub>. *Energy Fuels* 34(9):11299–11306
- Hwang ET, Lee JH, Chae YJ, Kim YS, Kim BC, Sang BI, Gu MB (2008) Analysis of the toxic mode of action of silver nanoparticles using stress-specific bioluminescent bacteria. *Small* 4(6):746–750
- Jourdin L, Burdyny T (2021) Microbial electrosynthesis: where do we go from here? *Trends Biotechnol* 39(4):359–369
- Jourdin L, Freguia S, Donose BC, Chen J, Wallace GG, Keller J, Flexer V (2014) A novel carbon nanotube modified scaffold as an efficient biocathode material for improved microbial electrosynthesis. *J Mater Chem A* 2(32):13093–13102
- Kim YK, Park SE, Lee H, Yun JY (2014) Enhancement of bioethanol production in syngas fermentation with *Clostridium ljungdahlii* using nanoparticles. *Bioresour Technol* 159:446–450
- Krieg T, Sydow A, Schroder U, Schrader J, Holtmann D (2014) Reactor concepts for bioelectrochemical syntheses and energy conversion. *Trends Biotechnol* 32(12):645–655
- Liu C, Gallagher JJ, Sakimoto KK, Nichols EM, Chang CJ, Chang MC, Yang P (2015) Nanowire-bacteria hybrids for unassisted solar carbon dioxide fixation to value-added chemicals. *Nano Lett* 15(5):3634–3639
- Liu C, Colón BC, Ziesack M, Silver PA, Nocera DG (2016) Water splitting-biosynthetic system with CO<sub>2</sub> reduction efficiencies exceeding photosynthesis. *Science* 352(6290):1210–1213
- Logan BE, Rabaey K (2012) Conversion of wastes into bioelectricity and chemicals by using microbial electrochemical technologies. *Science* 337(6095):686–690
- Marshall CW, Ross DE, Fichot EB, Norman RS, May HD (2013) Long-term operation of microbial electrosynthesis systems improves acetate production by autotrophic microbiomes. *Environ Sci Technol* 47(11):6023–6029
- Mohanakrishna G, Vanbroekhoven K, Pant D (2018) Impact of dissolved carbon dioxide concentration on the process parameters during its conversion to acetate through microbial electrosynthesis. *React Chem Eng* 3(3):371–378
- Myung J, Kim M, Pan M, Criddle CS, Tang SK (2016) Low energy emulsion-based fermentation enabling accelerated methane mass transfer and growth of poly(3-hydroxybutyrate)-accumulating methanotrophs. *Bioresour Technol* 207:302–307
- Nevin KP, Hensley SA, Franks AE, Summers ZM, Ou J, Woodard TL, Snoeyenbos-West OL, Lovley DR (2011) Electrosynthesis of organic compounds from carbon dioxide is catalyzed by a diversity of acetogenic microorganisms. *Appl Environ Microbiol* 77(9):2882–2886
- Patil SA, Arends JB, Vanwonterghem I, van Meerbergen J, Guo K, Tyson GW, Rabaey K (2015) Selective enrichment establishes a stable performing community for microbial electrosynthesis of acetate from CO<sub>2</sub>. *Environ Sci Technol* 49(14):8833–8843
- Prevosteau A, Carvajal-Arroyo JM, Ganigue R, Rabaey K (2020) Microbial electrosynthesis from CO<sub>2</sub>: forever a promise? *Curr Opin Biotechnol* 62:48–57
- Rodrigues RM, Guan X, Iñiguez JA, Estabrook DA, Chapman JO, Huang S, Sletten EM, Liu C (2019) Perfluorocarbon nanoemulsion promotes the delivery of reducing equivalents for electricity-driven microbial CO<sub>2</sub> reduction. *Nat Catal* 2(5):407–414
- Salehizadeh H, Yan N, Farnood R (2020) Recent advances in microbial CO<sub>2</sub> fixation and conversion to value-added products. *Chem Eng J* 390:124584
- Song TS, Zhang H, Liu H, Zhang D, Wang H, Yang Y, Yuan H, Xie J (2017) High efficiency microbial electrosynthesis of acetate from carbon dioxide by a self-assembled electroactive biofilm. *Bioresour Technol* 243:573–582
- Tian S, He J, Huang H, Song TS, Wu X, Xie J, Zhou W (2020) Perovskite-based multifunctional cathode with simultaneous supplementation of substrates and electrons for enhanced microbial electrosynthesis of organics. *ACS Appl Mater Interfaces* 12(27):30449–30456
- Xue X, Liu Z, Cai W, Cui K, Guo K (2022) Porous polyurethane particles enhanced the acetate production of a hydrogen-mediated microbial electrosynthesis reactor. *Bioresour Technol Rep* 18:101073

- Zhang T, Nie H, Bain TS, Lu H, Cui M, Snoeyenbos-West OL, Franks AE, Nevin KP, Russell TP, Lovley DR (2013) Improved cathode materials for microbial electrosynthesis. *Energy Environ Sci* 6(1):217–224
- Zhu H, Shanks BH, Heindel TJ (2008) Enhancing CO-water mass transfer by functionalized MCM41 nanoparticles. *Ind Eng Chem Res* 47(20):7881–7887

## Publisher's Note

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

**Submit your manuscript to a SpringerOpen<sup>®</sup> journal and benefit from:**

- Convenient online submission
- Rigorous peer review
- Open access: articles freely available online
- High visibility within the field
- Retaining the copyright to your article

---

Submit your next manuscript at ► [springeropen.com](https://www.springeropen.com)

---