Efficient conversion of bicarbonate (HCO_3^-) to acetate and simultaneous heavy metal Cr(VI) removal in photo-assisted microbial electrosynthesis systems combining $\text{WO}_3/\text{MoO}_3/\text{g-C}_3\text{N}_4$ heterojunctions and *Serratia marcescens* electrotroph

Liping Huang^{a,*}, Shiping Song^a, Zhenghong Cai^a, Peng Zhou^b, Gianluca Li Puma^{c,*}

^aKey Laboratory of Industrial Ecology and Environmental Engineering, Ministry of Education (MOE), School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, China

^bCollege of Chemistry, Dalian University of Technology, Dalian, 116024, China

^cEnvironmental Nanocatalysis & Photoreaction Engineering, Department of Chemical Engineering, Loughborough University, Loughborough LE11 3TU, United Kingdom

Corresponding authors:

lipinghuang@dlut.edu.cn (L. Huang)

g.lipuma@lboro.ac.uk (G. Li Puma)

The authors declare no competing financial interest.

Abstract

The removal of the hazardous heavy metal Cr(VI) in water and the simultaneous

production of acetate from the reduction of inorganic carbon (HCO_3^-) is demonstrated in a photo-assisted microbial electrosynthesis (MES) system incorporating $\text{WO}_3/\text{MoO}_3/\text{g-C}_3\text{N}_4$ Z-scheme heterojunctions and *Serratia marcescens* Q1 electrotoph cathode. The rates of acetate production (6.1 ± 0.3 mg/L/h) and Cr(VI) removal (4.5 ± 0.1 mg/L/h) recorded at a circuital current of 2.8 ± 0.1 A/m² were 2.4-fold (acetate production), 1.7-time (Cr(VI) removal) and 1.6-fold (circuital current) of those in the controls recorded in the absence of $\text{WO}_3/\text{MoO}_3/\text{g-C}_3\text{N}_4$, and 1.6-fold (acetate production) and 1.8-time (circuital current) of those in the absence of both Cr(VI) and $\text{WO}_3/\text{MoO}_3/\text{g-C}_3\text{N}_4$. Photogenerated $\text{WO}_3/\text{MoO}_3/\text{g-C}_3\text{N}_4$ conduction bands electrons favored both direct or indirect (via *S. marcescens*) reductions of Cr(VI) and H^+ , with the latter producing H_2 which was further metabolized by *S. marcescens* with HCO_3^- to yield acetate. The higher circuital current drawn under photoirradiation conditions refilled the photo-generated valence band holes in the semiconductor and provided the driving force for the reduction reactions. This study provides an alternative and feasible approach for achieving complete removal of toxic heavy metal from water and industrial waters with simultaneous conversion of inorganic carbon to key block chemicals.

Keywords: microbial electrosynthesis system; photo-assisted $\text{WO}_3/\text{MoO}_3/\text{g-C}_3\text{N}_4$; acetate production; Cr(VI) removal; circuital current

1 Introduction

Microbial electrosynthesis (MES) systems, which use whole electrotrophs as

biological catalysts have recently emerged as attractive and novel routes for the conversion of inorganic carbon such as bicarbonate (HCO_3^-) or carbon dioxide (CO_2) and for the synthesis of building block chemicals [1-2]. In these processes electrotrophs play a key role as electron acceptors in the reductive microbial transformation of HCO_3^- or CO_2 to chemicals. These electrons may originate indirectly from the assimilation of soluble electron carrier donors, for example via H_2 , or directly via cathodic electron transfer in MES. Specifically, the yield of a chemical product such as acetate may be favored by increasing the circuital current of the MES cell and thus the availability of cathodic electrons [2]. In turn, the circuital current may be further augmented by combination of the MES with bioremediation processes including perchlorate reduction, denitrification and removal of many heavy metals [3-4]. For example, many industrial processes such as electroplating, tannery, paint, wood, chromite ores and water cooling systems produce heavy metals rich wastewaters containing very low organic loads [5-7], in addition to releasing large amounts of inorganic carbon. Recently, the feasibility of MES of acetate from CO_2 sequestration as HCO_3^- and simultaneous removal of heavy metals Cd(II) or Cu(II) from heavy metal-contaminated and organics-barren waters and wastewaters has been demonstrated [8-9]. However, in this combined remediation MES process it is crucial to understand how the circuital cathodic electrons are competitively taken by the electrons acceptor species, i.e., the electrotrophs, protons and heavy metal ions.

One effective strategy to increase the circuital current and therefore the rates of chemicals and heavy metals reduction would be to craft the cathode of the MES with

light responsive photocatalytic semiconductor materials. These light active materials under artificial or solar light irradiation can feed photogenerated conduction band electrons to the electrotrophs and heavy metals ions and often reduce the cathode interfacial resistance and thus increase the cell external circuital current [10]. For this purpose, graphitic carbon nitride (g-C₃N₄), has been proposed as an effective, low-cost, highly stable, visible-light responsive semiconductor photocatalyst with excellent reduction properties (band gap about 2.7 eV; conduction band edge position of -1.2 eV vs. standard hydrogen electrode, SHE) [11]. Moreover, g-C₃N₄ when combined with WO₃ and MoO₃ (WO₃/MoO₃/g-C₃N₄) creates a Z-scheme heterojunction, which achieves efficient separation of the photo-generated electrons and holes and higher circuital currents. This strategy has been shown to improve the rates of biochemical reduction of HCO₃⁻ and the production of acetate by the non-photosynthetic *Serratia marcescens* Q1 electrotroph under anaerobic conditions [12].

Within this overarching context, this study examines the simultaneous process of environmental remediation of water from heavy metals and conversion of CO₂ to key block chemicals. The removal of the hazardous heavy metal Cr(VI) in water and the simultaneous production of acetate from the reduction of inorganic carbon (HCO₃⁻) is demonstrated in a photo-assisted MES system incorporating WO₃/MoO₃/g-C₃N₄ heterojunctions and *S. marcescens* Q1 electrotroph cathode. The underlying mechanism of the reactions and the competition between heavy metals and electrotrophs for the cathodic and photogenerated conduction bands electrons are

investigated while the stability and long-term performance of the cell is demonstrated over multiple operational cycles.

2 Materials and methods

2.1. WO_3/MoO_3 , $g-C_3N_4$ and $WO_3/MoO_3/g-C_3N_4$ synthesis and photocathodes preparation

The $g-C_3N_4$ was obtained as described by Shi et al. [11]. The loading procedure onto a graphite felt cathode and the amount loaded ($WO_3/MoO_3/g-C_3N_4$ equal to 1.43 mg/cm² with (WO_3/MoO_3)/ $g-C_3N_4$ ratio of 19.3% by weight) was as previously reported [12]. The physical and chemical characteristics of the abiotic $WO_3/MoO_3/g-C_3N_4$ loaded cathode determined by X-ray diffraction, photo-luminescence spectra, X-ray photoelectron spectroscopy, and UV-vis diffuse reflectance spectroscopy have been previously reported by our group [12].

2.2. Microbial photoelectrochemical reactor, electrotrough inoculation and operation

Each microbial photoelectrochemical reactor was made from two cubic polymethyl methacrylate blocks containing hollow cylindrical anodic and cathodic chambers (diameter 3 cm, volume 28 mL, working volume 26 mL). The dual chambers were ionically connected by a cation exchange membrane (CMI-7000 Membranes International, Glen Rock, NJ) which sufficiently prevented $Cr_2O_7^{2-}$ and product CH_3COO^- anions migration [13-16]. The reactors comprised $WO_3/MoO_3/g-C_3N_4$ graphite felt cathodes and carbon rods anodes. A saturated

calomel reference electrode (SCE, +241 mV vs. SHE) was placed in the cathodic chamber and all electrode potentials were reported vs. SHE.

The cathode was inoculated with *S. marcescens* Q1, a nonphotosynthetic electrotroph capable of producing acetate from inorganic carbon under anaerobic conditions, which was originally isolated from other bioelectrochemical systems [12,17-18]. Prior to the electrotroph inoculation, the catholyte in the cathodic chamber containing NaHCO₃ (2.0 g/L), NH₄Cl (0.11 g/L), KH₂PO₄ (0.012 g/L), vitamins 0.6 mL/L, mineral 0.6 mL/L and K₂Cr₂O₇ (170 or 339 mg/L, equal to 60 or 120 mg/L Cr(VI)), was sparged with N₂ gas for 15 min to remove the residual oxygen. Then, the electrotroph harvested after 24 h incubation in a sterile medium was inoculated into the cathodic chamber with a final OD₆₀₀ of 0.35. This optical density was selected as a tradeoff between efficient biocatalysis and light absorption on the photo-assisted cathode surface [19]. After gentle shaking of the reactors at 30 rpm for 15 min, the inoculated electrotroph was strongly adsorbed onto the WO₃/MoO₃/g-C₃N₄ graphite felt cathodes, since the catholyte effluent contained negligible bacteria at OD₆₀₀. As a consequence, acetate production and Cr(VI) removal throughout this investigation was attributed primarily to the contribution exerted by the electrotroph adsorbed onto the cathodic biofilm, while the contribution from the planktonic cells was considered negligible. Bacterial inoculation, reactor operation, and solution replacements were performed in an anaerobic glove box (YQX-II, Xinmiao, Shanghai) appropriately equipped with conducting wires connected to an external potentiostat (BioLogic, VSP, France) to guarantee the required continuous anaerobic conditions in the cathodic

chamber [20]. The survival of the *S. marcescens* species in the presence of the photocatalyst under light irradiation conditions was negligibly affected [12]. The initial concentration of Cr(VI) in the catholyte was varied between 0, 60 and 120 mg/L to determine its impact on both the kinetics of acetate and residual H₂ productions, and the kinetics of Cr(VI) removal. The conductivity in catholyte was regulated to 103 mS/cm with the addition of 0.6 M KCl [12]. The anolyte in the abiotic anode was made by a 50 mM phosphate buffer (pH 5.8) to prevent pH changes due to hydrolysis and the consequent effect on cathode performance during an experimental operational time of 12 h [1-2,12,18]. The anolyte was daily refreshed in experiments lasting more than 24 h to guarantee its pH stability. The catholyte pH was also set to 5.8 to avoid unwanted effect due to pH imbalances among the chambers. This pH was selected since it favors the *S. marcescens* activity in MES [12,18] and hydrogen evolution which is further needed for the microbial reduction of inorganic carbon [1,12]. The cathode potential was kept constant at -1.1 V to favor the production of acetate in the MES [21]. The cathodic chamber was irradiated by a 100 W iodine tungsten lamp producing an incident photon irradiance of 23.3 mW/cm² (simulated sunlight). The thermal heat produced by the lamp was continuously removed by a cooling fan. The temperature of the reactors was kept at 22 ± 3°C [12,22-23]. The long-term stability of the photo-assisted biocathode MES was assessed by performing up to 10 multiple cycles of fed-batch operation of the MES cell, with catholyte refreshment after completion of each cycle lasting 36 h. In addition, experiments with periodical addition of bicarbonate and Cr(VI) (up to 14

days) were operated to explore the impact of acetate accumulation during long term operation of the MES cells. In these experiments 3.0 mL of catholyte was replaced every 2 days with equal volume of mixed solution of NaHCO_3 and $\text{K}_2\text{Cr}_2\text{O}_7$ to reestablish the initial concentrations of inorganic carbon to 2.0 g/L and that of Cr(VI) to 60 mg/L. All experiments were performed in triplicates.

Six control experiments were performed: The first one (abiotic control) was operated in the absence of electrotroph inoculum using the $\text{WO}_3/\text{MoO}_3/\text{g-C}_3\text{N}_4$ photo-assisted cathode (abiotic PC) to determine the impact exerted by the electrotroph on the production of acetate and removal of Cr(VI). The second was operated using the biotic graphite felt cathode without photoirradiation (biotic GFC) to determine the influence of light irradiation or $\text{WO}_3/\text{MoO}_3/\text{g-C}_3\text{N}_4$ on system performance. The third was operated with the abiotic graphite felt cathode (abiotic GFC) to establish the impact of the $\text{WO}_3/\text{MoO}_3/\text{g-C}_3\text{N}_4$ photocatalyst. The fourth with the photo-assisted biocathode (OCC-PC), and the fifth with the biotic graphite felt cathode without photoirradiation (OCC-biotic GFC), were operated under open circuit conditions (OCC) to evaluate the impact of the electrochemical process. The sixth was operated in the absence of Cr(VI) to study the role of Cr(VI) on acetate and hydrogen production.

2.3. Characterization and electrochemical measurement

The surface morphology of the photo-assisted biocathodes in the presence/absence of Cr(VI) were examined by a SEM (Nova NanoSEM 450, FEI

company, USA) equipped with an EDS (X-MAX 20-50 mm², Oxford Instruments, UK). The photocatalytic activity of the photo-assisted biocathodes in a solution of 1.0 M Na₂SO₄ at an incident photon irradiance of 23.3 mW/cm² was examined by monitoring the photocurrent using a potentiostat (BioLogic, VSP, France) [12].

The electrochemical performance of the photo-assisted biocathode in the presence/absence of Cr(VI) was evaluated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). CV was conducted in the range from -1.2 V to 0.8 V at a scan rate of 0.1 mV/s through a potentiostat (BioLogic, VSP, France). Peak heights and midpoint potentials were obtained from the first derivative of CVs (DCVs) by calculating the slope of each data using the central difference quotient. EIS was carried out at -1.1 V vs. SHE in the frequency range from 100 kHz to 0.01 Hz with an amplitude of 5 mV. Both CV and EIS were performed with a three-electrode system as previously reported [22-23]. Zsimpwin software was used to calculate the equivalent circuit and the values of the different resistances.

2.4. Analysis and calculations

The concentration of acetate in the catholyte and the residual concentration of hydrogen in the headspace of the cathodic chamber were determined by gas chromatography (GC7900, Tianmei, China). Acetate production was expressed in terms of either concentration (mg/L) or average production rate (mg/L/h) while the H₂ production rate was determined by normalizing the volume to the volume of the catholyte and to the operational time (m³/m³/d). The concentration of inorganic

carbon in the catholyte was determined using standard methods [24], and the inorganic carbon consumption rate was calculated by taking the difference between the initial and the final inorganic carbon concentrations in the catholyte, divided by the volume of the catholyte and the operational time (mg/L/h). Analysis of total chromium and soluble Cr(VI) was referred to the standard methods [24]. The residual dissolved Cr(III) was then calculated as the difference between total chromium and soluble Cr(VI), whereas the Cr(VI) removal rate (mg/L/h) was defined as the difference between the initial and the final Cr(VI) concentrations in the catholyte divided by the operational time.

The coulombic efficiencies relative to the production of acetate (CE_{acetate}), the residual hydrogen gas (CE_{H_2}) and the reduction of Cr(VI) (CE_{Cr}) were calculated according to Eqs. 1 – 3:

$$CE_{\text{acetate}} = \frac{8 \times n_a \times F}{\int_0^t I dt} \times 100\% \quad (1)$$

$$CE_{\text{H}_2} = \frac{2 \times n_b \times F}{\int_0^t I dt} \times 100\% \quad (2)$$

$$CE_{\text{Cr}} = \frac{3 \times n_c \times F}{\int_0^t I dt} \times 100\% \quad (3)$$

Where n_a (mol) is the amount of acetate, n_b (mol) is the amount of H_2 and n_c (mol) is the amount of Cr(VI), I (A) is the current, F (96485 C/mole electron) is the Faraday constant and t is the operation time (s).

3 Results and discussion

3.1 MES photo-assisted biotic cathode performance and comparison with the controls

Figure 1 shows the rates of production of acetate and H₂, the rate of Cr(VI) removal and the circuit current of the cell under biotic, abiotic and under OCC, in the presence and in the absence of light irradiation. In the absence of Cr(VI), the highest rate of acetate production was obtained in the biotic PC as expected, since all cathodic and photoinduced valence-band electrons were utilized by the electrotroph to drive the synthesis of acetate. In such case, the reduction of HCO₃⁻ by *S. marcescens* to acetate was driven by simultaneous direct electron transfer (via the external circuit) and indirect electron transfer mechanisms (via H₂ metabolism) [12].

In the presence of Cr(VI) and as the concentration of heavy metal was increased, the production rate of acetate in the biotic PC progressively decreased due to the competitive reduction reaction of Cr(VI) to Cr(III) (Reaction 4) forming Cr(OH)₃ deposits (Reaction 5). At an initial Cr(VI) concentration of 60 mg/L and in the biotic PC, the acetate production rate was 6.1 ± 0.3 mg/L/h (Fig. 1A), the Cr(VI) removal rate was 4.5 ± 0.1 mg/L/h (Fig. 1C), the residual H₂ production rate was 0.0013 ± 0.0001 m³/m³/d (Fig. 1B) and the circuit current was 2.8 ± 0.1 A/m² (Fig. 1D). These were 2.4-fold (acetate production), 1.7-fold (Cr(VI) removal) and 1.6-fold (circuit current) higher than the corresponding values observed in the control experiments using the biotic GFC at the same initial Cr(VI) concentration (Fig. 1A, C and D). These were also 1.6-fold (acetate production) (Fig. 1A) and 1.8-time (circuit current) (Fig. 1D) higher values than those determined in the absence of both Cr(VI) and WO₃/MoO₃/g-C₃N₄ photocatalyst. A higher observed acetate production rate (Fig. 1A) consistent with a lower residual H₂ production rate (Fig. 1B), also confirmed the

effective utilization of the cathodically evolved H_2 (Reaction 6) for indirect electron transfer to the *S. marcescens* electrotroph and its further use for the reduction of HCO_3^- to acetate (Reaction 7) through the Wood-Ljungdahl pathway [1-2]. Collectively, these results demonstrate that it is possible to achieve simultaneous efficient acetate production and Cr(VI) removal with relatively high circuital currents using this biotic PC. The improved rate of acetate production (6.1 ± 0.3 mg/L/h vs. 2.5 ± 0.1 mg/L/h) (Fig. 1A) and circuital current (2.8 ± 0.1 A/m² vs. 1.7 ± 0.04 A/m²) (Fig. 1D) observed with the biotic PC, in comparison with the results using the biotic GFC, can be confidently associated to the favorable impact of the photo-generated valence-band electrons and photo-improved circuital currents.

The apparent Cr(VI) removal rate of 4.5 ± 0.1 mg/L/h (removal efficiency: $90 \pm 3\%$) in the PC combined with *S. marcescens* was 1.3 – 2.0 folds higher than the rates observed using *Stenotrophomonas* sp. YS1, *Stenotrophomonas maltophilia* YS2, *Serratia marcescens* YS3, *Achromobacter xylosoxidans* YS8, or *Shewanella oneidensis* MR-1 cathodes in bioelectrochemical systems without photoirradiation and during a short operational period of 4 – 5 h [25-26] and 15-fold higher than the rates observed in plant-sediment bioelectrochemical systems [27]. Moreover, the apparent Cr(VI) removal rate in this study was 2.6 – 7.5 folds higher than the rates reported for *S. marcescens* UC-2 or UC-6 [28-31]. Although photocatalytic processes using g-C₃N₄ have reported higher Cr(VI) removal rates [32], it should be noted that these consume large amounts of chemicals and do not produce valuable products.

Under OCC, the biotic PC delivered a higher Cr(VI) removal rate (1.0 ± 0.04

mg/L/h) than in the controls using the biotic GFC (0.8 ± 0.03 mg/L/h) ($p < 0.05$) (Fig. 1C), confirming that a fraction of the photo-generated electrons was also used for the direct or the indirect (via electrotroph) reduction of Cr(VI) on the MES cathode. This was further evidenced by the higher Cr(VI) removal rate (3.5 ± 0.04 mg/L/h vs. 1.9 ± 0.06 mg/L/h) (Fig. 1C) and circuital current (1.75 ± 0.04 A/m² vs. 1.16 ± 0.03 A/m²) (Fig. 1D) observed in the abiotic PC compared to the abiotic GFC. The essential need of an electron flow for the production of acetate by the *S. marcescens* electrotroph in this MES was clearly demonstrated by the absence of acetate production in the OCC experiments, with or without photoirradiation (Fig. 1A).

Doubling the initial Cr(VI) concentration (120 mg/L rather than 60 mg/L), a higher fraction of cathodic electrons was used towards the reduction of Cr(VI) (6.3 ± 0.1 mg/L/h) (Fig. 1C) and this in turn caused a reduction of the rates of acetate production (4.4 ± 0.2 mg/L/h) (Fig. 1A) and inorganic carbon consumption (25.1 ± 0.6 mg/L/h) (Fig. S1). This aspect can strategically be used to tailor the performance of the cell towards either heavy metal removal or acetate production. The higher circuital current observed under these conditions in comparison to the controls, using either the biotic GFC at the same Cr(VI) concentration of 120 mg/L or the abiotic PC at lower Cr(VI) concentrations of 0 – 60 mg/L (Fig. 1D), confirmed the favorable role of the WO₃/MoO₃/g-C₃N₄ heterojunction as an efficient electron transfer photocatalyst. Many other investigations have reported the favorable impact exerted by the presence of supplementary catholyte electron acceptors on the circuital current of many other bioelectrochemical systems [33-35]. Notably, the results (Fig. 1A, at

Cr-120) shows that the irradiation of the $\text{WO}_3/\text{MoO}_3/\text{g-C}_3\text{N}_4$ cathode with light can completely offset the competitive action of Cr(VI) reduction on the rate of acetate production (photo-assisted and Cr(VI) of 120 mg/L: 4.4 ± 0.2 mg/L/h; no photo and Cr(VI): 3.9 ± 0.4 mg/L/h. $p = 0.38 > 0.05$), demonstrating the tremendous role exerted by the present biotic PC in mitigating the competitive action of Cr(VI) towards the influx of cathodic electrons, even at such very high heavy metal concentration. It is therefore possible to envisage that such MES process could be used for the sustainable conversion of CO_2 (as bicarbonate) to acetate with simultaneous environmental remediation of heavy metals.

Here Fig. 1

3.2 Reaction mechanisms

In such photo-assisted MES system, it has been shown that the irradiation of the $\text{WO}_3/\text{MoO}_3/\text{g-C}_3\text{N}_4$ heterojunction creates well separated conduction band electrons and semiconductors holes following a Z-scheme mechanism [12]. Thus, it can be hypothesized that the photogenerated conduction band electrons favors both the direct (via electrons flowing in from the external circuit) or the indirect (via *S. marcescens*) reduction of Cr(VI) (Reactions 4 – 5) and H^+ , with the latter producing H_2 (Reaction 6) which is further metabolized by *S. marcescens* with HCO_3^- to yield acetate (Reaction 7). In parallel, the photo-generated holes in the semiconductor valence band are refilled by a fraction of the electrons travelling from the anodic chamber through the external circuit to the cathode of the bioelectrochemical cell. The electrons also favor

not only the cathodic direct or indirect (via *S. marcescens*) reduction of Cr(VI) and H⁺, but also the *S. marcescens* direct (Reaction 8) or indirect (via H₂) (Reactions 6 – 7) utilization for acetate production, as summarized in Fig. 2. As a consequence, this biotic PC of MES can achieve simultaneous efficient acetate production and Cr(VI) removal.

Here Fig. 2

3.3 Kinetics of MES of acetate over a prolonged operational time and at various initial Cr(VI) concentrations

The rates of acetate production and HCO₃⁻ consumption, over a prolonged operational time up to 14 h and at an initial concentration of Cr(VI) of 60 mg/L, progressively increased (Fig. 3A) as the concentration of Cr(VI) in solution decreased, finally approaching 6.0 ± 0.4 mg/L/h (acetate production) and 31.9 ± 1.5 mg/L/h (NaHCO₃ consumption) after 14 h. The fraction of inorganic carbon converted to acetate (Reactions 7 – 8) accounted to 55 – 62% by mole of the inorganic carbon consumed. The remaining 38 – 45% of inorganic carbon consumed was mainly ascribed to supporting bacterial growth and intracellular metabolisms, similar to the

behavior observed in other autotrophic or mixotrophic electrotrophy bioelectrochemical systems [25-26]. The acetate accumulation rate was marginally higher than the rate observed at an initial Cr(VI) concentration of 120 mg/L (Fig. 3E) and significantly higher than the controls using the biotic GFC (Fig. 3A and E) at the same operational times. The rate of acetate production was also appreciably higher than the 3.4 ± 0.1 mg/L/h recorded in the absence of both Cr(VI) and photoirradiation (Fig. S2). This confirmed the significant role exerted by the supplementary valence band electrons produced by photoirradiation of the semiconductor heterojunction in mitigating the competitive role of Cr(VI) reduction on the production of acetate. The higher rate of acetate production observed was reasonably correlated to a higher rate of HCO_3^- consumption (Fig. 3A and E) and a lower rate of Cr(VI) removal (Fig. 3B and F) over the operational time.

The relative distribution of the cathodic electrons over the underlying reduction processes occurring in either the biotic PC or the biotic GFC is key to elucidate the role exerted by each reacting species. The invariable higher cathodic electrons observed in the biotic PC (Fig. 3C and G) relative to the biotic GFC (Fig. 3D and H) (Cr(VI) of 60 mg/L: $0.20 \pm 0.02 - 0.54 \pm 0.02$ C vs. $0.12 \pm 0.01 - 0.34 \pm 0.03$ C; Cr(VI) of 120 mg/L: 0.52 ± 0.02 C – 1.31 ± 0.06 C vs. $0.26 \pm 0.01 - 0.68 \pm 0.02$ C), reveals a higher reductive driving force for the conversion of both Cr(VI) to Cr(III) (Fig. 3B and F) and HCO_3^- to acetate (Fig. 3A and E) under photoirradiation conditions during the entire operational period. These results also support the results shown in Fig. 1A and C. The insignificant difference ($p = 0.31$) among the cathodic

electrons observed at a Cr(VI) of 60 mg/L (0.49 ± 0.01 C, Fig. 3C) and at 120 mg/L (0.52 ± 0.02 C, Fig. 3G) at the same operational time of 12 h, implies equal driving force with negligible effects arising from using different Cr(VI) concentrations.

Here Fig. 3

3.4 Morphology of the photo-assisted biocathode

The morphology and elemental composition of the cathodes after 36 h operation was observed by SEM/EDS (Fig. 4 and Table S1). The rod-shaped *S. marcescens* bacillus formed large irregular-shaped agglomerates on both the bare (Fig. 4D) and the WO₃/MoO₃/g-C₃N₄ coated (Fig. 4A) electrodes. EDS analysis of the elemental composition taken on the bacterial agglomerates indicated the presence of the same elements, but in different ratios (Fig. 4C and F; Table S1) however, the W and Mo signals were detected only in the coated electrode (Fig. 4B; Table S1). The Cr signal was detected in all samples, indicating that Cr(IV) reduction occurred in both the surface of the *S. marcescens* and on the surfaces of both bare and WO₃/MoO₃/g-C₃N₄ coated cathodes. The elemental signals (Table S1) were higher on the WO₃/MoO₃/g-C₃N₄ coated cathode (Fig. 4B and C) than on the bare cathode (Fig. 4E and F), indicating a much higher reduction activity in the presence of the semiconductors heterojunction consistent with the results in Figs. 1 and 3. Moreover within the WO₃/MoO₃/g-C₃N₄ coated cathode, the Cr signal was higher on the *S. marcescens* surface (1.4% (mol/mol), Fig. 4C and Table S1) rather than on the semiconductor bare surface (0.5% (mol/mol), Fig. 4B and Table S1), illustrating the

concerted role exerted by both the WO₃/MoO₃/g-C₃N₄ heterojunction and the *S. marcescens* species towards the reduction of Cr(VI), consistent with the results shown in Figs. 1 and 3.

Here Fig. 4

3.5 CV and EIS characterization

The electrochemical performance of the biotic and abiotic GFC, and of the biotic and abiotic PC in the presence/absence of Cr(VI) was evaluated by CV and EIS. Comparing the biotic PC and the biotic GFC at 60 mg/L Cr(VI), the inorganic carbon reduction onset potential (−0.52 V vs. −0.33 V) and the reduction peak potential (−0.62 V vs. −0.52 V) shifted to more positive values, and the reduction peak current significantly increased (−0.10 mA vs. −0.42 mA) (Fig. 5A; Table S2). Thus, an increase of the rate of HCO₃[−] reduction in the presence of WO₃/MoO₃/g-C₃N₄ was observed (Figs. 1 and 3). At a higher Cr(VI) concentration (120 mg/L), the inorganic carbon reduction onset potential shifted slightly to more negative values (−0.37 V) due to a decrease of the rate of HCO₃[−] reduction, but remained appreciably more positive than the values recorded with the biotic GFC at a lower Cr(VI) of 60 mg/L (−0.52 V) or the value in the absence of both Cr(VI) and WO₃/MoO₃/g-C₃N₄ (−0.46 V) [12]. This is in agreement with the kinetics results (Figs. 1 and 3) and confirms the robustness of the biotic PC for efficient production of acetate from inorganic carbon reduction, even under harsh Cr(VI) stress conditions.

With regard to Cr(VI) reduction, the presence of WO₃/MoO₃/g-C₃N₄ invariably

positively affected the Cr(VI) reduction onset potential (0.46 V vs. 0.37 V), reduction peak potential (0.25 V vs. -0.01 V), and reduction peak current (-0.45 mA vs. -0.27 mA) (Fig. 5A; Table S2). In the abiotic controls, Cr(VI) reduction onset potential, reduction peak potential and reduction peak current in both PC and GFC were invariably low. A more positive reduction onset potential on the biotic electrode indicated a decrease in the overall free energy of the electron transfer reaction, mainly due to bacterial interactions with the electrode surface [36]. The more positive reduction set potential observed at a Cr(VI) initial concentration of 120 mg/L rather than at 60 mg/L (0.52 V vs. 0.46 V) suggests that less energy was required for the reduction of Cr(VI) at this higher concentration. This behavior has also been observed in other bioelectrochemical systems for the reduction of Cr(VI), Au(III), Co(II) and Fe(III) [17,20,36].

Accordingly, DCV plots demonstrated a broader redox active potential range (-0.21 ~ -0.53 V vs. -0.41 ~ -0.62) with a more positive midpoint potential (-0.41 V vs. -0.55 V) for the biotic PC, compared to the biotic GFC control (Fig. 5B; Table S2), indicating more adaptable and changeable components in the cathodic biofilm which correlated with extracellular electron transfer in the presence of photoirradiation. This behavior was similar to the adaptation of *Geobacter sulfurreducens* in response to different external applied potentials [37].

The EIS spectra (Fig. 5C) were analyzed and were represented by equivalent circuits (Fig. S3). The presence of light irradiation and WO₃/MoO₃/g-C₃N₄ significantly decreased the charge transfer resistance (R_{ct} , 110 Ω vs. 67 Ω) and slightly

increased the solution and electrode resistance (R_s , 3.8 Ω vs. 8.1 Ω) and the diffusion resistance (R_{dif} , 42 Ω vs. 61 Ω) at the same initial Cr(VI) concentration (60 mg/L) (Fig. 5C; Table S3). The increase in R_s and R_{dif} was associated to the formation of insoluble and non-conductive $\text{Cr}(\text{OH})^{2+}$, $\text{Cr}(\text{OH})_2^+$ and $\text{Cr}(\text{OH})_3$ on the electrode surface and/or within the microorganism suggesting some degree of mass transfer limitation. This behavior has also been reported in other bioelectrochemical systems [17,20,26,33,38]. Similar trends were observed in the abiotic controls but with higher R_{ct} (126 Ω vs. 87 Ω), and lower R_s (3.1 Ω vs. 6.6 Ω) and R_{dif} (36 Ω vs. 49 Ω). The smaller increase in R_s and R_{dif} in the abiotic controls was associated to the lower rate of product formation.

A higher Cr(VI) concentration (120 mg/L) invariably increased the R_s (8.1 Ω vs. 11.9 Ω), the R_{ct} (67 Ω vs. 82 Ω) and in particular the R_{dif} (61 Ω vs. 315 Ω), confirming the controlling role exerted by Cr(VI) and its reduction products, reducing electron transfer towards the bio-reduction of inorganic carbon to acetate, as observed in the results shown in Figs. 1 and 3. Moreover, in terms of microbial metabolism, the higher Cr(VI) toxicity at 120 mg/L might have triggered a defense mechanism on the electrotrophic *S. marcescens* which resulted in a significant increase of R_{dif} in relation to the other resistances. These results corroborates with that of others obtained with different biocathodes exposed to Cr(VI), Co(II), Cu(II) or Cd(II) stress conditions at progressively increasing heavy metal concentrations or at higher cathode potentials without photoirradiation [17,20,39-40].

Here Fig. 5

3.6 Stability assessment

The stability of the biotic PC was assessed by performing consecutive batch cycles. Each cycle lasted 36 h and the initial concentration of Cr(VI) in the catholyte (120 mg/L) was refreshed at the end of each cycle. The results shows that acetate production ($5.6 \pm 0.2 - 6.1 \pm 0.2$ mg/L/h) (Fig. 6A), residual H₂ ($0.018 \pm 0.001 - 0.020 \pm 0.001$ m³/m³/d) (Fig. 6A), and Cr(VI) removal ($3.2 \pm 0.02 - 3.3 \pm 0.0$ mg/L/h) (Fig. 6C) stabilized within the initial 4 operational cycles. These results correlated well with the negligible changes observed in current density ($2.3 \pm 0.1 - 2.4 \pm 0.1$ A/m²) (Fig. 6C), CE_{acetate} ($56.9 \pm 0.2 - 57.7 \pm 0.3\%$), CE_{Cr} ($13.7 \pm 0.6 - 14.2 \pm 0.5\%$) and CE_{H_2} ($0.12 \pm 0.03 - 0.13 \pm 0.01\%$) (Fig. 6D), and leaching of W ($0.25 \pm 0.02 - 1.35 \pm 0.03\%$) and Mo ($1.0 \pm 0.01 - 2.6 \pm 0.01\%$) (Fig. 6B) within the same operational period. Accordingly, progressively smaller notable variations of the CVs were observed (Fig. 6E; Table S4) despite the somewhat increase in the internal resistances (R_s , R_{ct} and R_{dif}) (Fig. 6F; Table S4).

A prolonged operation to 10 cycles invariably decreased the rates of both acetate and residual H₂ production by 25% (Fig. 6A), the Cr(VI) removal rate by 27% (Fig. 6C) and the observed circuitial current by 17% (Fig. 6C), consistently with a decrease in the catalytic activities as observed in the CVs results (Fig. 6E; Table S4) and in accordance with an apparent increase in the internal resistance (EIS results, Fig. 6F; Table S4).

Moreover the reduction of W ($0.05 \pm 0.01\%$) and Mo ($0.3 \pm 0.01\%$) leaching in the catholyte, as well as, a slight increase in the effluent pH (Fig. 6B) at the end of the

10th operating cycle, was consistent with a gradual accumulation of non-conductive Cr deposits over the cathode, which progressively created a physical barrier to further diminishing W and Mo leaching (Fig. S4; Table S5). This phenomenon was similar to the adverse effects exerted by non-conductive Cr, Cd or Co deposits on the cathodes of other bioelectrochemical systems [8,17,20,26,38,40].

Here Fig. 6

3.7 MES performance with periodical addition of bicarbonate and Cr(VI)

In order to assess the stability of the biotic PC over continuous acetate accumulation, the catholyte was periodically supplemented with bicarbonate and Cr(VI) every two days to reestablish the original initial concentrations, up to a total operational period of 14 days. The results show that the MES cell accumulated acetate up to 1623 ± 17 mg/L at the end of day 14th almost following a linear path at a rate of 116 ± 1 mg/L/d (Fig. 7A). Concomitantly, steady reduction of HCO_3^- (478 ± 11 mg/L/d) (Fig. 7A) and Cr(VI) removal (40 ± 2 mg/L/d) (Fig. 7B) were observed during each operational interval. These results were 2.3-fold (acetate production), 1.2-fold (Cr(VI) removal) and 1.2-fold (HCO_3^- consumption) of those in the controls with biotic GFC (Fig. 7A and B), reflecting the crucial role exerted by the $\text{WO}_3/\text{MoO}_3/\text{g-C}_3\text{N}_4$ biocathode. This acetate production rate was appreciably higher than the 6 – 53 mg/L/d using other pure strains of *Sporomusa* or *Moorella thermoautotrophica* on a reduced graphene oxide-coated copper foam composite cathode [41-43] or the 75 mg/L/d using *Clostridium ljungdahlii* catalyzed graphene

nanosheet-carbon nanotube cathode [44] at similar operational periods in the absence of heavy metals. Moreover, the Cr(VI) removal rate was significantly higher than the 0.53 – 0.83 mg/L/d observed using *Shewanella oneidensis* MR-1, *S. putrefaciens* W3-18-1, *S. amazonensis* SB2B, *Shewanella sp.* ANA-3, *S. loihica* PV-4 or *Shewanella sp.* MR-4 cathodes at a similar operational period of 3 h and without the functional production of acetate [45].

A higher rate of acetate production (Fig. 7A) was closely correlated with a lower residual H₂ (Fig. 7C) and a lower pH in the catholyte (Fig. 7D), which contrasted sharply with a significantly lower production of acetate, a higher residual H₂ and a higher pH in the catholyte in the controls using the biotic GFC (Fig. 7A, C and D). Simultaneously, the concentration of dissolved Cr(III) in the catholyte increased up to 2.4 mg/L after 14-day operation (Fig. 7B) whereas W and Mo leaching sharply decreased (Fig. 7D) as previously explained.

The biotic PC still exhibited a uniform and reversible photocurrent response after 14-day operation (Fig. 7E). The 24% reduction of photocurrent after day 14th (Fig. 7E), closely correlated with the decrease of the residual H₂ production rate (Fig. 7C), implying a reduction of the rate of photo-induced valence band electrons, and thus lower H₂ evolution after this long operation. This also correlated with the formation of Cr deposits over the cathode shielding light absorption. Moreover, considering the negligible leaching of W and Mo at day 14th (Fig. 7D) and the generally observed irregular-shaped aggregates as non-conductive Cr signals on the electrode at prolonged operation time (Fig. S4), the progressive decrease in photocurrent might be

ascribed to a great extent to the increased resistance offered by the non-conductive Cr deposits on the cathode.

EIS analysis demonstrated the dominant and invariable role of the diffusional resistance of the reacting species, R_{dif} (50 – 178 Ω) over the increase in the value of R_{ct} (from 48 Ω to 83 Ω) and a slight increase in the R_s (6.5 – 14.1 Ω) during the entire 14 days operation (Fig. 7F; Table S6). The R_{dif} and R_{ct} values were appreciably lower than the values 195 – 303 Ω (R_{dif}) and 136 – 225 Ω (R_{ct}) observed during the same period from 4 to 14 days using the biotic GFC (Fig. 7F; Table S6).

The use of $\text{WO}_3/\text{MoO}_3/\text{g-C}_3\text{N}_4$ and *S. marcescens* catalyzed cathode was for the first time proven to improve simultaneous Cr(VI) removal and reduction of inorganic carbon, achieving 6.1 ± 0.3 mg/L/h (acetate production), 4.5 ± 0.1 mg/L/h (Cr(VI) removal) and 2.8 ± 0.1 A/m² (circuital current) in the MES under fed-batch operation. These values were 2.4-fold (acetate), 1.7-time (Cr(VI) removal) and 1.6-fold (circuital current) of those observed in the absence of $\text{WO}_3/\text{MoO}_3/\text{g-C}_3\text{N}_4$, and 1.6-fold (acetate production) and 1.8-time (circuital current) of those in the absence of both Cr(VI) and $\text{WO}_3/\text{MoO}_3/\text{g-C}_3\text{N}_4$. Under periodical addition of bicarbonate and Cr(VI) with a prolonged operation up to 14 days, simultaneous efficient acetate production (116 ± 1 mg/L/d) and Cr(VI) removal (40 ± 2 mg/L/d) was also observed, 2.3-time (acetate production) and 1.2-fold (Cr(VI) removal) of those in the controls with the biotic GFC.

The $\text{WO}_3/\text{MoO}_3/\text{g-C}_3\text{N}_4$ heterojunction has been previously proven to be highly efficient for the production of photo-induced conduction band electrons which were

utilized by the *S. marcescens* species, directly or indirectly (via H_2), for the production of acetate at relatively high rates [12]. Herein, in the presence of the highly toxic Cr(VI) heavy metal, both the photo-induced electrons and the circuital currents were utilized not only for the direct or indirect (via *S. marcescens*) reduction of Cr(VI) and H^+ , but also for the direct or indirect (via H_2) reduction of HCO_3^- by the *S. marcescens* (Fig. 2). The WO_3 and MoO_3 are inexpensive, bio-compatible and microbial friendly materials, particularly when compared to other semiconductor MES metals oxides of Cd, Ni or Bi, which in general exert significant microbial toxicity and poor stability in the catholyte after prolonged operation [46-48]. Alternatively, the WO_3 or MoO_2 can be combined with $g-C_3N_4$ or carbon nanodots to form Z-scheme heterojunctions achieving efficient abiotic photocatalytic oxidation of many recalcitrant organics or reduction of aqueous Cr(VI) [11,49-54]. The use of photo-assisted MES incorporating $WO_3/MoO_3/g-C_3N_4$ heterojunctions and self-replicated *S. marcescens* cathodes broadens the application horizon of $WO_3/MoO_3/g-C_3N_4$ heterojunctions as an attractive and environmental desirable process for the synthesis of acetate from inorganic carbon waste, particularly in conjunction with simultaneous removal/recovery of hazardous heavy metals from contaminated waters and wastewaters.

4. Conclusions

This study has examined the simultaneous process of environmental remediation of water from heavy metals and conversion of CO_2 to key block chemicals. It has

demonstrated that the incorporation of an efficient solar-responsive WO₃/MoO₃/g-C₃N₄ heterojunction and the combination of this with *S. marcescens* Q1 electrotoph results in a highly efficient and stable photo-biocathode which achieves enhanced simultaneous reduction of HCO₃⁻ and Cr(VI) over prolonged operation up to 14 days. This is accomplished via significant increases in the available external circuit current and photo-generated electrons over the efficient Z-scheme heterojunction. Moreover, the process can be tailored towards acetate production or heavy metal removal depending on the relative concentration of HCO₃⁻ and Cr(VI). This study has demonstrated that the incorporation of an efficient photo-assisted heterojunction in a MES cell provides an alternative and environmentally benign approach for achieving simultaneous efficient production of a key block chemical (acetate) and removal of heavy metals, opening up the feasibility of sustainable treatment of heavy metal contaminated waters and wastewaters fed by high loads of inorganic carbon.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors gratefully acknowledge financial support from the National Natural Science Foundation of China (No. 21777017).

References

- [1] K. Rabaey and R.A. Rozendal, Microbial electrosynthesis-revisiting the electrical route for microbial production, *Nature Rev. Microbiol.* 8 (2010) 706-716.
- [2] Y. Jiang, H.D. May, L. Lu, P. Liang, X. Huang, Z.J. Ren, Carbon dioxide and organic waste valorization by microbial electrosynthesis and electro-fermentation, *Water Res.* 149 (2019) 42-55.

- [3] C.S. Butler, P. Clauwaert, S.J. Green, W. Verstraete, R. Nerenberg, Bioelectrochemical perchlorate reduction in a microbial fuel cell, *Environ. Sci. Technol.* 44 (2010) 4685-4691.
- [4] H. Wang and Z.J. Ren, Bioelectrochemical metal recovery from wastewater: a review, *Water Res.* 66 (2014) 219-232.
- [5] C.E. Barrera-Diaz, V. Lugo-lugo, B. Bilyeu, A review of chemical, electrochemical and biological methods for aqueous Cr(VI) reduction, *J. Hazard. Mater.* 223-224 (2012) 1-12.
- [6] L. Dai, L. Cui, D. Zhou, J. Huang, S. Yuan, Resource recovery of Cr(VI) from electroplating wastewater: Laboratory and pilot-scale investigation using fibrous weak anion exchanger, *J. Taiwan Inst. Chem. E.* 54 (2015) 170-177.
- [7] T.C. Machado and M.A. Lansarin, Wastewater containing Cr(VI) treatment using solar tubular reactor, *Water Sci. Technol.* 74 (2016) 1698-1705.
- [8] X. Hou, L. Huang, P. Zhou, F. Tian, Y. Tao, G. Li Puma, Electrosynthesis of acetate from inorganic carbon (HCO_3^-) with simultaneous hydrogen production and Cd(II) removal in multifunctional microbial electrosynthesis systems (MES), *J. Hazard. Mater.* 371 (2019) 463-473.
- [9] J. Hou, L. Huang, P. Zhou, Y. Qian, N. Li, Understanding the interdependence of strain of electrotroph, cathode potential and initial Cu(II) concentration for simultaneous Cu(II) removal and acetate production in microbial electrosynthesis systems, *Chemosphere* 243 (2020) 125317.
- [10] X. Qi, Y. Ren, P. Liang, X. Wang, New insights in photosynthetic microbial fuel cell using anoxygenic phototrophic bacteria, *Bioresour. Technol.* 258 (2018) 310-317.
- [11] A. Shi, H. Li, S. Yin, J. Zhang, Y. Wang, H_2 evolution over g- $\text{C}_3\text{N}_4/\text{Cs}_x\text{WO}_3$ under NIR light. *Appl. Catal. B-Environ.* 228 (2018) 75-86.
- [12] Z. Cai, L. Huang, X. Quan, Z. Zhao, Y. Shi, G. Li Puma, Acetate production from inorganic carbon (HCO_3^-) in photo-assisted biocathode microbial electrosynthesis systems using $\text{WO}_3/\text{MoO}_3/\text{g-C}_3\text{N}_4$ heterojunctions and *Serratia marcescens* species, *Appl. Catal. B: Environ.* 267 (2020) 118611.
- [13] L. Huang, F. Tian, Y. Pan, L. Shan, Y. Shi, B.E. Logan, Mutual benefifits of acetate and mixed tungsten and molybdenum for their efficient removal in 40 L microbial electrolysis cells, *Water Res.* 162 (2019) 358-368.
- [14] L. Huang, L. Jiang, Q. Wang, X. Quan, J. Yang, L. Chen, Cobalt recovery with simultaneous methane and acetate production in biocathode microbial electrolysis cells, *Chem. Eng. J.* 253 (2014) 281-290.
- [15] L. Huang, B. Yao, D. Wu, X. Quan, Complete cobalt recovery from lithium cobalt oxide in self-driven microbial fuel cell-microbial electrolysis cell systems, *J. Power Sources* 259 (2014) 54-64.
- [16] Y. Qian, L. Huang, Y. Pan, X. Quan, H. Lian, J. Yang, Dependency of migration and reduction of mixed $\text{Cr}_2\text{O}_7^{2-}$, Cu^{2+} and Cd^{2+} on electric field, ion exchange membrane and metal concentration in microbial fuel cells, *Sep. Purif. Technol.* 192 (2018) 78-87.
- [17] L. Huang, Q. Wang, L. Jiang, P. Zhou, X. Quan, B.E. Logan, Adaptively evolving

- bacterial communities for complete and selective reduction of Cr(VI), Cu(II) and Cd(II) in biocathode bioelectrochemical systems, *Environ. Sci. Technol.* 49 (2015) 9914-9924.
- [18] Y. Qian, L. Huang, P. Zhou, F. Tian, G. Li Puma, Reduction of Cu(II) and simultaneous production of acetate from inorganic carbon by *Serratia marcescens* biofilms and plankton cells in microbial electrosynthesis systems, *Sci. Total Environ.* 666 (2019) 114-125.
- [19] E.M. Nichols, J.J. Gallagher, C. Liu, Y. Su, J. Resasco, Y. Yu, Y. Sun, P. Yang, M.C.Y. Chang, C.J. Chang, Hybrid bioinorganic approach to solar-to-chemical conversion, *Proc. Natl. Acad. Sci. USA.* 112 (2015) 11461-11466.
- [20] L. Huang, Y. Liu, L. Yu, X. Quan, G. Chen, A new clean approach for production of cobalt dihydroxide from aqueous Co(II) using oxygen-reducing biocathode microbial fuel cells, *J. Cleaner Prod.* 86 (2015) 441-446.
- [21] L. Jourdin, S. Freguia, V. Flexer, J. Keller, Bringing high-rate, CO₂-based microbial electrosynthesis closer to practical implementation through improved electrode design and operating conditions, *Environ. Sci. Technol.* 50 (2016) 1982-1989.
- [22] Q. Wang, L. Huang, X. Quan, G. Li Puma, Sequential anaerobic and electro-Fenton processes mediated by W and Mo oxides for degradation/mineralization of azo dye methyl orange in photo assisted microbial fuel cells, *Appl. Catal. B-Environ.* 245 (2019) 672-680.
- [23] Q. Wang, Z. Cai, L. Huang, Y. Pan, X. Quan, G. Li Puma, Intensified degradation and mineralization of antibiotic metronidazole in photo-assisted microbial fuel cells with Mo-W catalytic cathodes under anaerobic or aerobic conditions in the presence of Fe(III), *Chem. Eng. J.* 376 (2019) 119566.
- [24] American Public Health Association, American Water Works Association, Water Pollution Control Federation, Standard methods for the examination of water and wastewater, 20th ed., American Public Health Association, Washington, DC, 1998.
- [25] N. Xafenias, Y. Zhang, C.J. Banks, Enhanced performance of hexavalent chromium reducing cathodes in the presence of *Shewanella oneidensis* MR-1 and lactate, *Environ. Sci. Technol.* 47 (2013) 4512-4520.
- [26] H. Xue, P. Zhou, Huang L, Quan X, Yuan J. Cathodic Cr(VI) reduction by electrochemically active bacteria sensed by fluorescent probe. *Sensor Actuat. B-Chem.* 243 (2017) 303-310.
- [27] C. Cheng, Y. Hu, S. Shao, J. Yu, W. Zhou, J. Cheng, Y. Chen, S. Chen, J. Chen, L. Zhang, Simultaneous Cr(VI) reduction and electricity generation in plant-sediment microbial fuel cells (P-SMFCs): Synthesis of non-bonding CoO₄ nanowires onto cathodes, *Environ. Pollut.* 247 (2019) 647-657.
- [28] V. Campos, G. Escalante, J. Yáñez, C. Zaror, M. Mondaca, Isolation of arsenite-oxidizing bacteria from a natural biofilm associated to volcanic rocks of Atacama Desert, Chile. *J. Basic Microbiol.* 49 (2009) S93-S97.
- [29] V. Campos, R. Moraga, Í. Fernández, F. Yáñez, A. Valenzuela, M. Mondaca, Reduction of hexavalent chromium by *Serratia marcescens* immobilized on active carbon and their potential use in bioremediation, *Gayana* 77 (2013) 60-63.

- [30] J.P.F. de Bruijn and M.A. Mondaca, Chromate reduction by *Serratia marcescens* immobilized on activated carbon, *Toxicol. Environ. Chem.* 76 (2000) 125-135.
- [31] M. Mondaca, V. Campos, R. Moraga, C. Zaror, Chromate reduction in *Serratia marcescens* isolated from tannery effluent and potential application for bioremediation of chromate pollution, *Sci. World J.* 2 (2002) 972-977.
- [32] W. Song, P. Ge, Q. Ke, Y. Sun, F. Chen, H. Wang, Y. Shi, X. Wu, H. Lin, J. Chen, C. Shen, Insight into the mechanisms for hexavalent chromium reduction and sulfisoxazole degradation catalyzed by graphitic carbon nitride: The *Yin* and *Yang* in the photo-assisted processes, *Chemosphere* 221 (2019) 166-174.
- [33] C. He, Z. Mu, H. Yang, Y. Wang, Y. Mu, H. Yu, Electron acceptors for energy generation in microbial fuel cells fed with wastewaters: a mini-review, *Chemosphere* 140 (2015) 12-17.
- [34] W. Li, H. Yu, Z. He, Towards sustainable wastewater treatment by using microbial fuel cells-centered technologies, *Energy Environ. Sci.* 7 (2014) 911-924.
- [35] X. Liu, W. Li, H. Yu, Cathodic catalysts in bioelectrochemical systems for energy recovery from wastewater, *Chem. Soc. Rev.* 43 (2014) 7718-7745.
- [36] J. Varia, S.S. Martínez, S.V. Orta, S. Bull, S. Roy, Bioelectrochemical metal remediation and recovery of Au^{3+} , Co^{2+} and Fe^{3+} metal ions, *Electrochim. Acta* 95 (2013) 125-131.
- [37] X. Zhu, M.D. Yates, B.E. Logan, Set potential regulation reveals additional oxidation peaks of *Geobacter sulfurreducens* anodic biofilms, *Electrochem. Commun.* 22 (2012) 116-119.
- [38] Q. Wang, L. Huang, Y. Pan, X. Quan, G. Li Puma, Impact of Fe(III) as an effective mediator for enhanced Cr(VI) reduction in microbial fuel cells: Reduction of diffusional resistances and cathode overpotentials, *J. Hazard. Mater.* 321 (2017) 896-906.
- [39] J. Shen, L. Huang, P. Zhou, X. Quan, G. Li Puma, Correlation between circuit current, Cu(II) reduction and cellular electron transfer in EAB isolated from Cu(II)-reduced biocathodes of microbial fuel cells, *Bioelectrochemistry* 114 (2017) 1-7.
- [40] L. Huang, L. Jiang, Q. Wang, X. Quan, J. Yang, L. Chen, Cobalt recovery with simultaneous methane and acetate production in biocathode microbial electrolysis cells, *Chem. Eng. J.* 253 (2014) 281-290.
- [41] N. Aryal, P.L. Tremblay, D.M. Lizak, T. Zhang, Performance of different *Sporomusa* species for the microbial electrosynthesis of acetate from carbon dioxide, *Bioresour. Technol.* 233 (2017) 184-190.
- [42] N. Aryal, L.L. Wan, M.H. Overgaard, A.C. Stoot, Y.M. Chen, P.L. Tremblay, T. Zhang, Increased carbon dioxide reduction to acetate in a microbial electrosynthesis reactor with a reduced graphene oxide-coated copper foam composite cathode, *Bioelectrochemistry* 128 (2019) 83-93.
- [43] S. Chen, Y. Fang, X. Jing, H. Luo, J. Chen, S. Zhou, Enhanced electrosynthesis performance of *Moorella thermoautotrophica* by improving cell permeability, *Bioelectrochemistry* 121 (2018) 151-159.
- [44] S. Han, H. Liu, C. Zhou, H. Ying, Growth of carbon nanotubes on graphene as

- 3D biocathode for NAD⁺/NADH balance model and high-rate production in microbial electrochemical synthesis from CO₂, J. Mater. Chem. A. 7 (2019) 1115-1123.
- [45] L. Hsu, S.A. Masuda, K.H. Nealson, M. Pirbazari, Evaluation of microbial fuel cell *Shewanella* biocathodes for treatment of chromate contamination, RSC Adv. 2 (2012) 5844-5855.
- [46] Y. Hou, Y. Gan, Z. Yu, X. Chen, L. Qian, B. Zhang, L. Huang, J. Huang, Solar promoted azo dye degradation and energy production in the bio-photoelectrochemical system with a g-C₃N₄/BiOBr heterojunction photocathode, J. Power Sources 371 (2017) 26-34.
- [47] H. Nie, T. Zhang, M. Cui, H. Lu, D.R. Lovley, T.P. Russell, Improved cathode for high efficient microbial-catalyzed reduction in microbial electrosynthesis cells, Phys. Chem. Chem. Phys. 15 (2013) 14290-14294.
- [48] K.K. Sakimoto, A.B. Wong, P. Yang, Self-photosensitization of nonphotosynthetic bacteria for solar-to-chemical production, Science 351 (2016) 74-77.
- [49] B. Chai, C. Liu, J. Yan, Z. Ren, Z. Wang, In-situ synthesis of WO₃ nanoplates anchored on g-C₃N₄ Z-scheme photocatalysts for significantly enhanced photocatalytic activity, Appl. Surf. Sci. 448 (2018) 1-8.
- [50] K. Chen, X. Zhang, X. Yang, M. Jiao, Z. Zhou, M. Zhang, D. Wang, X. Bu, Electronic structure of heterojunction MoO₃/g-C₃N₄ catalyst for oxidative desulfurization, Appl. Catal. B-Environ. 238 (2018) 263-273.
- [51] J. Jia, C. Jiang, X. Zhang, P. Li, J. Xiong, Z. Zhang, T. Wu, Y. Wang, Urea-modified carbon quantum dots as electron mediator decorated g-C₃N₄/WO₃ with enhanced visible-light photocatalytic activity and mechanism insight, Appl. Surf. Sci. 495 (2019) 143524.
- [52] S. Patnaik, G. Swain, K.M. Parida, Highly efficient charge transfer through a double Z-scheme mechanism by a Cu-promoted MoO₃/g-C₃N₄ hybrid nanocomposite with superior electrochemical and photocatalytic performance, Nanoscale 10 (2018) 5950-5964.
- [53] J. Zhang, Y. Ma, Y. Du, H. Jiang, D. Zhou, S. Dong, Carbon nanodots/WO₃ nanorods Z-scheme composites: remarkably enhanced photocatalytic performance under broad spectrum, Appl. Catal. B-Environ. 209 (2017) 253-264.
- [54] J. Zhang, Y. Guo, Y. Xiong, D. Zhou, S. Dong, An environmentally friendly Z-scheme WO₃/CDots/CdS heterostructure with remarkable photocatalytic activity and antiphotocorrosion performance, J. Catal. 356 (2017) 1-13.

Figure captions

Fig. 1 Comparison of acetate production (A), residual hydrogen (B), Cr(VI) removal (C) and circuit current (D) in the photo-assisted biocathode (PC) and in the controls of biotic graphite felt cathode without photoirradiation (biotic GFC), abiotic photo-assisted cathode (abiotic PC), abiotic graphite felt cathode (abiotic GFC), photo-assisted biocathode (OCC-PC) or biotic graphite felt cathode without

photoirradiation (OCC-biotic GFC) under open circuit conditions (operational time: 12 h).

Fig. 2 Schematic processes of Cr(VI) removal and production of acetate in the *S. marcescens* catalyzed cathode of MES incorporating with either bare graphite felt (A) or WO₃/MoO₃/g-C₃N₄ (C), or in the absence of both WO₃/MoO₃/g-C₃N₄ and Cr(VI) (B).

Fig. 3 Time course of acetate production and bicarbonate consumption (A and E), Cr(VI) removal and residual H₂ (B and E), and distribution of cathodic electrons either in the biotic photo-assisted cathode (PC) (C and G) or biotic graphite felt cathode (GFC) (D and H) at an initial Cr(VI) of 60 mg/L (A – D) or 120 mg/L (E – H). A higher initial Cr(VI) required more time for complete removal, and operational periods of 36 h at a Cr(VI) initial concentration of 120 mg/L (E – H) and 14 h at a Cr(VI) initial concentration of 60 mg/L (A – D) were determined from preliminary experiments.

Fig. 4 Morphological SEM/EDS observation on the cathodes after 36 h operation for either the photo-assisted WO₃/MoO₃/g-C₃N₄ cathode (A – C) or the bare graphite felt cathode (D – F) in the presence of *S. marcescens* electrotrroph. EDS for a region without (B and E) or with (C and F) *S. marcescens* (initial Cr(VI) concentration: 120 mg/L).

Fig. 5 Comparison of CV (A), derivative CV (DCV) (B) and EIS (C) on either the biotic or abiotic photo-assisted WO₃/MoO₃/g-C₃N₄ cathodes (PC), or the biotic graphite felt cathodes (GFC) at various initial Cr(VI) of 0, 60 or 120 mg/L.

Fig. 6 Acetate production and residual H₂ (A), W and Mo leaking and effluent pH (B), Cr(VI) removal and circuit current (C), coulombic efficiencies for acetate production (CE_{acetate}), Cr(VI) removal (CE_{Cr}) and residual H₂ (CE_{H_2}), CV (E), and EIS (F) as a function of the number of cycle (each cycle: 36 h; initial Cr(VI): 120 mg/L).

Fig. 7 Comparison of acetate production and residual bicarbonate (A), residual Cr(VI) or Cr(III) (B), residual H₂ (C), W and Mo leaching and effluent pH (D), photocurrent (E) and EIS (F) at different operational intervals with periodical addition of bicarbonate and Cr(VI) in the the biotic photo-assisted WO₃/MoO₃/g-C₃N₄ cathodes (PC), or the biotic graphite felt cathodes (GFC) (Black arrows indicated the points of bicarbonate or Cr(VI) addition).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Supporting Information

Efficient conversion of bicarbonate (HCO_3^-) to acetate and simultaneous heavy metal Cr(VI) removal in photo-assisted microbial electrosynthesis systems combining $\text{WO}_3/\text{MoO}_3/\text{g-C}_3\text{N}_4$ heterojunctions and *Serratia marcescens* electrotroph

Liping Huang^{a,*}, Shiping Song^a, Zhenghong Cai^a, Peng Zhou^b, Gianluca Li Puma^{c,*}

^aKey Laboratory of Industrial Ecology and Environmental Engineering, Ministry of Education (MOE), School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, China

^bCollege of Chemistry, Dalian University of Technology, Dalian, 116024, China

^cEnvironmental Nanocatalysis & Photoreaction Engineering, Department of Chemical Engineering, Loughborough University, Loughborough LE11 3TU, United Kingdom

Corresponding authors:

lipinghuang@dlut.edu.cn (L. Huang)

g.lipuma@lboro.ac.uk (G. Li Puma)

Tables: 6

Figures: 4

Pages: 8

Table S1 EDS analysis on element composition of the deposits at different locations of the photo-associated WO₃/MoO₃/g-C₃N₄ or bare graphite felt biocathodes (initial Cr(VI): 120 mg/L; operational time: 36 h).

Condition	Location	Element	Percent		Location	Percent		
			(w/w)	(mol/mol)		(w/w)	(mol/mol)	
Photo-assisted WO ₃ /MoO ₃ /g-C ₃ N ₄ biocathode	WO ₃ /MoO ₃ /g-C ₃ N ₄ covered but no biofilm	C	76.5	86.7	Biofilm covered	70.1	79.4	
		N	7.2	5.3		---	---	
		O	8.3	7.0		7.4	7.2	
		Cr	2.3	0.5		5.5	1.4	
		Mo	2.8	0.4		---	---	
		W	3.0	0.2		---	---	
		Na	---	---		2.1	1.3	
		P	---	---		12.9	9.7	
		K	---	---		2.0	1.1	
		Total	100	100			100	100
Bare graphite felt biocathode	No biofilm covered	C	88.2	92.9	Biofilm covered	73.5	80.6	
		O	10.4	6.8		12.5	12.3	
		Cr	1.4	0.4		2.1	0.9	
		Na	---	---		2.3	1.3	
		P	---	---		6.7	3.6	
		K	---	---		2.9	1.4	
				Total		100	100	

Table S2 CV and derivative CV (DCV) data on the biotic photo-assisted WO₃/MoO₃/g-C₃N₄ (PC) or graphite felt (GFC) cathodes, or the abiotic photo-assisted WO₃/MoO₃/g-C₃N₄ (PC-abiotic) or graphite felt (GFC-abiotic) cathodes at various initial Cr(VI) concentrations.

	Conditions	Reduction onset potential (V, vs. SHE)	Reduction peak potential (V, vs. SHE)	Reduction peak current (mA)	Midpoint potential (V, vs. SHE)	Range of redox activity (V, vs. SHE)
Cr(VI)	PC-60	0.46	0.25	−0.45	0.37	0.55 ~ 0.23
	PC-120	0.52	0.23	−0.52	0.38	0.66 ~ 0.24
	GFC-60	0.37	−0.01	−0.27	0.09	0.29 ~ −0.01
	GFC-abiotic-60	0.34	0.05	−0.20	---	---
	PC-abiotic-60	0.41	0.06	−0.38	---	---
HCO ₃ [−]	PC-0	−0.31	−0.54	−0.60	−0.39	−0.15 ~ −0.55
	PC-60	−0.33	−0.52	−0.42	−0.41	−0.21 ~ −0.53
	PC-120	−0.37	−0.56	−0.38	−0.47	−0.32 ~ −0.55
	GFC-60	−0.52	−0.62	−0.10	−0.55	−0.41 ~ −0.62
	GFC-60-abiotic	---	---	---	---	---
	PC-60-abiotic	---	---	---	---	---

Table S3 EIS parameters obtained from Nyquist plots on the biotic photo-assisted WO₃/MoO₃/g-C₃N₄ (PC) or graphite felt (GFC) cathodes, or the abiotic photo-assisted WO₃/MoO₃/g-C₃N₄ (PC-abiotic) or graphite felt (GFC-abiotic) cathodes at various initial Cr(VI) concentrations.

Conditions	R_s (Ω)	R_{ct} (Ω)	R_{dif} (Ω)
PC-0	5.1	32	30
PC-60	8.1	67	61
PC-120	11.9	82	315
GFC-60	3.8	110	42
PC-abiotic-60	6.6	87	49
GFC-abiotic-60	3.1	126	36

Table S4 CV data and the corresponding EIS parameters obtained from Nyquist plots as a function of number of cycle

Conditions		Reduction onset potential (V, vs. SHE)	Reduction peak potential (V, vs. SHE)	Reduction peak current (mA)	R_s (Ω)	R_{ct} (Ω)	R_{dif} (Ω)
1 st cycle	Cr(VI)	0.52	0.23	-0.52	11.8	82	315
	HCO ₃ ⁻	-0.37	-0.56	-0.38			
4 th cycle	Cr(VI)	0.51	0.22	-0.39	17.7	121	525
	HCO ₃ ⁻	-0.38	-0.57	-0.28			
10 th cycle	Cr(VI)	0.49	0.20	-0.23	22.5	150	729
	HCO ₃ ⁻	-0.40	-0.59	-0.23			

Table S5 EDS analysis on element composition of the deposits on the photo-associated WO₃/MoO₃/g-C₃N₄ biocathodes after 1st cycle and 10th cycle operations.

Condition	Location	Elements	Percent		Location	Percent	
			(w/w)	(mol/mol)		(w/w)	(mol/mol)
1 st cycle	WO ₃ /MoO ₃ /g-C ₃ N ₄ covered but no biofilm	C	76.5	86.7	Biofilm covered	70.1	79.4
		N	7.2	5.3		---	---
		O	8.3	7.0		7.4	7.2
		Cr	2.3	0.5		5.5	1.4
		Mo	2.8	0.4		---	---
		W	3.0	0.2		---	---
		Na	---	---		2.1	1.3
		P	---	---		12.9	9.7
10 th cycle	No biofilm covered	K	---	---	Biofilm covered	2.0	1.1
		Total	100	100		100	100
		C	75.8	86.0		66.8	78.3
		N	8.4	6.0		---	---
		O	8.1	6.8		8.4	7.8
		Cr	3.4	0.8		7.1	1.5
		Mo	1.8	0.3		---	---
		W	2.4	0.2		---	---
		Na	---	---		2.4	1.3
		P	---	---		13.3	10.0
		K	---	---		2.2	1.1
		Total	100	100		100	100

Table S6 EIS parameters obtained from Nyquist plots on the biotic photo-assisted WO₃/MoO₃/g-C₃N₄ (PC) or graphite felt (GFC) cathodes at various operational times under periodical addition of bicarbonate and Cr(VI).

Condition	R_s (Ω)	R_{ct} (Ω)	R_{dif} (Ω)
PC-0 d	6.5	48	50
PC-4 d	9.3	66	135
PC-8 d	11.4	71	154
PC-14 d	14.1	83	178
GFC-0 d	3.5	100	47
GFC-4 d	8.8	136	195
GFC-8 d	10.6	187	234
GFC-14 d	16.1	225	303

Fig. S1 Comparison of bicarbonate consumption in the photo-assisted biocathode (PC) and in the controls of graphite felt biocathode (GFC), abiotic photo-assisted cathode (abiotic PC), abiotic graphite felt cathode (abiotic GFC), photo-assisted biocathode (OCC-PC) or graphite felt biocathode (OCC-GFC) under open circuit conditions (operational time: 12 h).

Fig. S2 Time course of acetate production (A) and bicarbonate consumption (B) in the biotic photo-assisted cathode (PC) or biotic graphite felt cathode (GFC) in the absence of Cr(VI).

R_s : solution and electrode resistance;
 R_{ct} : charge transfer resistance;
 R_{dif} : diffusion resistance;
 CPE: constant phase element.

Fig. S3 Equivalent circuits

Fig. S4 Morphological SEM observation on photo-assisted *S. marcescens* catalyzed electrodes (A), and EDS determination on the sites of either $\text{WO}_3/\text{MoO}_3/\text{g-C}_3\text{N}_4$ (B) or *S. marcescens* (C) covered photo-assisted electrodes at 10th cycle operation.