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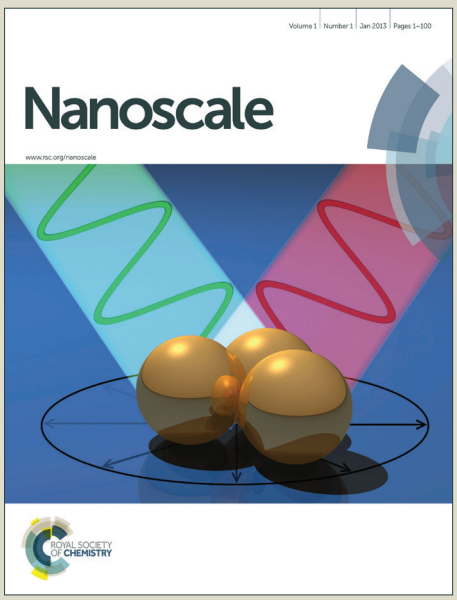

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ARTICLE

Facilitated Extracellular Electron Transfer of *Shewanella loihica* PV-4 by Antimony-doped Tin Oxide Nanoparticles as Active Microelectrodes

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Dissimilatory metal reducing bacteria are capable of extracellular electron transfer (EET) to insoluble metal oxides as external electron acceptor for their anaerobic respiration, which is recognized as important energy-conversion process in natural and engineered environments, such as mineral cycling, bioremediation, and microbial fuel/electrolysis cells. However, the low EET efficiency remains one of the major bottlenecks in its practical applications. We report firstly that the microbial current generated by *Shewanella loihica* PV-4 (*S. loihica* PV-4) could be greatly improved that is up to ca. 115 fold, by adding antimony-doped tin oxide (ATO) nanoparticles in the electrochemical reactor. The results demonstrate that the biocompatible, electrically conductive ATO nanoparticles, acted as active microelectrodes, could facilitate the formation of cells/ATO composite biofilm and create the reduction of the outer membrane c-type cytochromes (OM c-Cyts) that are beneficial for the electron transfer from cells to electrode. Meanwhile, synergetic effect between the participation of OM c-Cyts and the accelerated EET mediated by cell-secreted flavins may play an important role for the enhanced current generation in the presence of ATO nanoparticles. Moreover, it is worth noting that the TCA cycle in *S. loihica* PV-4 cells is activated by adding ATO nanoparticles, even if potential poised at +0.2 V, thereby also improving the EET process. The results presented here may provide a simple and effective strategy to boost EET of *S. loihica* PV-4 cells, which is conducive to providing potential applications in bioelectrochemical systems.

Introduction

Extracellular electron transfer (EET) is a process through which electrogenic microbes, such as genus *Shewanella*, transport metabolically generated electrons to extracellular solid metal oxides or charged electrodes which serve as external electron acceptor.[1-3] Microbial EET is an important process involved in versatile natural processes as biogeochemical cycling of minerals, bioremediation,[4-7] and practical applications as microbial fuel cells (MFCs) and microbial electrolysis cells (MECs).[8-11] However, the limited EET efficiency and poor controllability in actual systems are still main bottlenecks for its practical applications. It is therefore highly desirable to develop a useful and simple approach for accelerating anodic EET.

Generally, EET of *Shewanella* could be proceeded either directly by physical contact with electron acceptors via the outer membrane c-type cytochromes (OM c-Cyts) or indirectly through self-secreted soluble flavins.[12-14] In recent years, considerable efforts have been devoted to develop simple, effective strategies for improving EET efficiency, including the modification of microbes,[15-17] the addition of soluble mediators,[18-20] the decoration of the electrodes,[21-24] and the introduction of conductive and biocompatible nanomaterials. Among them, the addition of nanomaterials has been recognized as a simple method to significantly improve the EET efficiency. For example, the microbial current of *Shewanella loihica* PV-4 (*S. loihica* PV-4) exhibited a fiftyfold increase after adding α-Fe_2O_3 nanocolloids.[25] And Fe_3O_4/Au nanocomposites were developed to enhance the c-type cytochromes (c-Cyts) wire efficiency of *Shewanella oneidensis* MR-1 (*S. oneidensis* MR-1), showing a 22-fold increase of microbial current.[26] The biogenic FeS as extracellular long-distant electron-transfer conduits improved the microbial current of *S. loihica* PV-4 by two orders of magnitude.[27] Moreover, the assembled reduced-graphene-oxide biofilm delivered a 25-fold growth in the oxidant current of *S. oneidensis* MR-1 in MFC.[28] However, a shortcoming of these inorganic nanomaterials is their poor

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† Electronic Supplementary Information (ESI) available: (1) TEM images of the ATO nanoparticles added in the experiment; (2) experimental set up; (3) comparison of whole cell cyclic voltammetry (CV) with different concentration of ATO nanoparticles; (2) Nyquist plots of cells in the presence and absence of ATO nanoparticles; (3) SEM images of cells fixed on electrode with and without ATO nanoparticles; (4) CV curves of wild type and Δ2525 mutant cells. See DOI: 10.1039/x0xx00000x

conductivity, which may to some extent limit the efficiency of electron transfer.

Transparent conducting oxides (TCO), such as indium-tin oxide (ITO) and antimony-doped tin oxide (ATO), have been attracted much attention owing to their high electrical conductivity, optical transparency, and promising applications in electrochemical devices.[29-31] In particular, TCO have been examined as substrates for adsorption of biomolecules, which may offer the possibility for developing bio-electrochemical applications. For instance, Frasca et al.[32] demonstrated the stable immobilization of c-Cyts in mesoporous ITO film, which served as biosensor for detecting superoxide anions. As an indispensable member of TCO, ATO has good biocompatibility which is verified by the absorption of DNA nanostructures[33] or c-Cyts[34] to porous ATO without destruction of their structure and electron transfer functionality. Although ITO glass has been widely used as working electrodes to study the EET of electrogenic microbes, there is no report yet on the introduction of TCO nanoparticles as microelectrodes into electrochemical cell to improve microbial EET in vivo.

Here, we report a simple and effective strategy to substantially enhance EET process of *S. loihica* PV-4 as a model electrogenic microbe by adding ATO nanoparticles with 5~10 nm size (Fig. S1), acted as active microelectrodes, with concentration of 2 mM in electrochemical reactor. The ATO nanomaterials for improvement of microbial EET were selected based on the following rationales: (1) low cost and good biocompatibility, (2) good electrical conductivity, (3) strong interaction between ATO and protein. As expected, the microbial current of *S. loihica* PV-4 cells shows a ca. 115-fold increase in the presence of ATO nanoparticles. It is proposed that the added ATO nanoparticles could not only act as microelectrodes for electron transfer from cells to electrode in which OM c-Cyts play a key role, but also facilitate the biofilm formation, which are beneficial for EET process. In particular, EET mediated through cell-secreted flavins is accelerated due to the altering redox state of OM c-Cyts by adding ATO nanoparticles. Besides, the TCA cycle in the cells is activated in the presence of ATO nanoparticles, thus facilitating the microbial EET process. The introduction of conducting inorganic oxide nanoparticles may provide a simple, cost-effective way to enhance the EET efficiency of the electrogenic microbes.

Results and discussion

In our experiment, to observe the EET of *S. loihica* PV-4 cells, we used a single-chamber, three electrode system consisting of Ag|AgCl (saturated KCl) and a platinum wire as reference and counter electrodes, respectively, with sodium lactate (10 mM) as the carbon source and electron donor. An optical transparent ITO glass with a surface area of 1.8 cm^2 was used as the working electrode, placed on the bottom of the reactor (Fig. S2). Fig. 1a shows the representative anodic currents generated in this system by *S. loihica* PV-4 cells at an applied potential of +0.2 V (vs. Ag/AgCl) with and without the addition of ATO nanoparticles. Upon injecting *S. loihica* PV-4 cells into the system, an oxidation current was generated instantly in the absence of ATO nanoparticles, and then reached a constant value of 0.86 μA after 10 h of operation (Fig. 1a, dashed curve). If ATO nanoparticles with concentration of 2 mM were added and completely precipitated on the surface of ITO electrode, a current generated upon injecting cells and reached a maximum value of 98.9 μA after cells cultivation for 2 h (Fig. 1a, solid curve), which is a ca. 115-fold increase, demonstrating that ATO nanoparticles could significantly boost electron transfer of microbes. In the presence of ATO nanoparticles, as shown in Fig. 1a (solid curve), no current generated until the injection of cells, confirming that the current generation originates from microbial activity of *S. loihica* PV-4 cells. The quantity of electric charge (Q) was calculated by integrating each I-t curve with respect to time (t), as shown in Fig. 1b. It can be seen that the transfer of charge in the presence of ATO nanoparticles (solid curve) is much higher than that in the absence of ATO nanoparticles (dashed curve). These results confirm that the increased microbial current of *S. loihica* PV-4 is attributed to the added ATO nanoparticles.

To elucidate the actual role of ATO nanoparticles, the whole-cell cyclic voltammetry (CV) was measured with and without the addition of ATO nanoparticles. As shown in Fig. 2a,

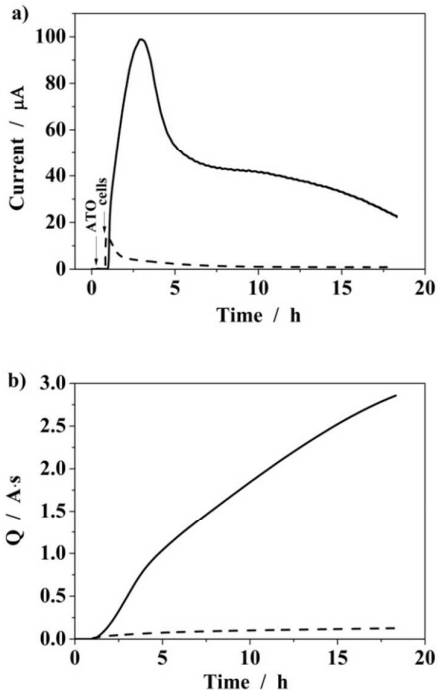

Fig. 1 (a) Current (I) versus time (t) curves with (solid curve) and without (dashed curve) the addition of ATO nanoparticles (2 mM). (b) Quantity of electric charge (Q) versus time (t) curves with (solid curve) and without (dashed curve) the addition of ATO nanoparticles.

the cells cultured on ITO electrode exhibit a redox peak with a midpoint potential (E_m) of approximately -0.24 V (vs. Ag/AgCl) in the absence of ATO nanoparticles (dashed curve), which agrees well with the reported E_m values of OM c-Cyts.[35-38] In the presence of ATO nanoparticles, however, the E_m of OM c-Cyts appears at approximately -0.08 V (vs. Ag/AgCl) as shown in Fig. 2a (solid curve), which has a significant positive shift of 160 mV. As reported previously,[39] the E_m of OM c-Cyts is dependent on their redox state, and its positive shift may reflect the production of the reduced form of OM c-Cyts, and stabilize the reduced hemes of OM c-Cyts in a feedback manner.

Besides, the different pulse voltammogram (DPV), which is capable of dectecting redox species present in trace amounts in biological system, was conducted to examine the redox characteristics of cell-secreted flavin molecules. As shown in Fig. 2b, the DPV curve obtained in the presence of ATO nanoparticles (solid curve), compared with that in the absence of ATO nanoparticles (dashed curve), has two anodic peaks, which are assigned to the OM c-Cyts (more positive one) and the self-secreted flavins (more negative one).[13, 40] Baseline subtracted DPVs for the flavins and OM c-Cyts related peaks are given in Fig. 2c and Fig. 2d, respectively. In the presence of ATO nanoparticles, the observed peak potential (E_p) of flavins (Fig. 2c) performs a positive shift of 27 mV from -382 mV (dashed curve) to -355 mV (solid curve), and the E_p assigned to OM c-Cyts (Fig. 2d) shifts positively from -199 mV (dashed curve) to -149 mV (solid curve). Based on the "bound-flavin cofactor" model,[41-43] the cell-secreted flavins, acted as redox cofactors of OM c-Cyts, are bound to OM c-Cyts protein with reduced hemes accompanying the positive shift of E_p assigned to flavins, but are released after the oxidation of the hemes in OM c-Cyts protein. Accordingly, the positive shift of E_p assigned to both flavins and OM c-Cyts indicates the formation of flavin-OM c-Cyts cofactor in the presence of ATO nanoparticles.

Taken together, the OM c-Cyts are in their reduced form in the presence of ATO nanoparitcles, which may have interacted strongly with flavins secreted by cells to form flavin-OM c-Cyts cofactor with good stabilization, thus resulting in a faster one electron transfer mediated by semiquinoe. In addition, it was observed that the biocatalytic current of *S. loihica* PV-4 cells increased, while the intensity of the redox peaks assigned to OM c-Cyts decreased in the presence of ATO nanoparticles (Fig. 2a). These results illustrate that ATO nanoparticles play an important role in improving EET process which is distinct from the function of α-Fe_2O_3 nanocolloids reported previously.[44]

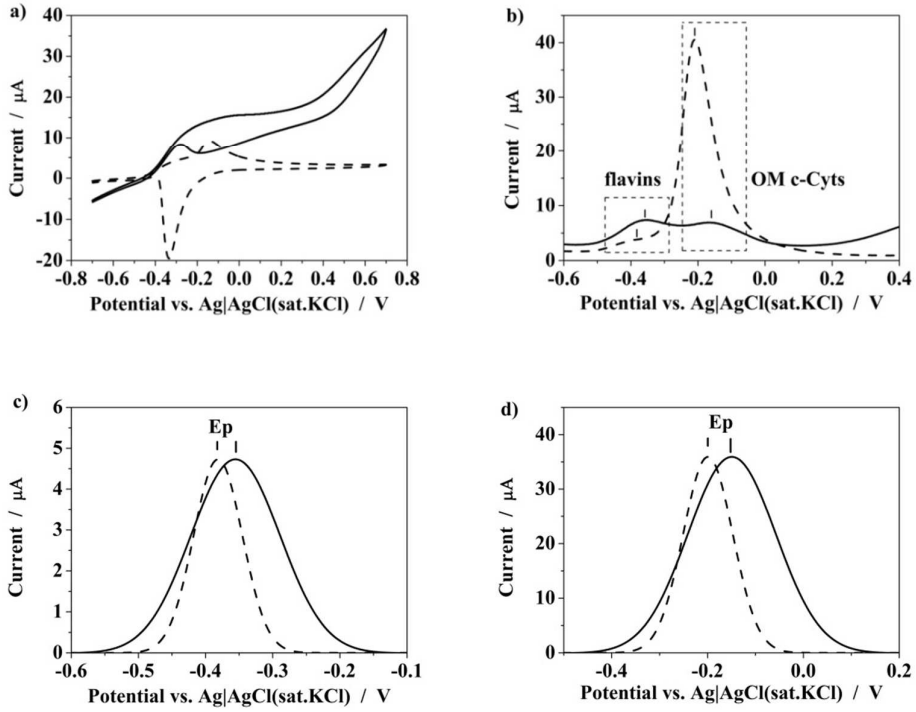

Fig. 2 (a) Cyclic voltammetry curves of *S. loihica* PV-4 cells at a scanning rate of 1 mV • s^{-1} in the presence (solid curve) and the absence (dashed curve) of ATO nanoparticles. (b) Differential pulse voltammograms of *S. loihica* PV-4 cells respectively cultured in the presence (solid curve) and the absence (dashed curve) of ATO nanoparticles. Baseline-subtracted DPV for flavins (c) and OM c-Cyts (d) in the presence (solid curve) and the absence (dashed curve) of ATO nanoparticles.

The SEM image (Fig. 3a) reveals that the thick composite biofilm of ATO nanoparticles (B) and *S. loihica* PV-4 cells (C) is formed at the surface of ITO electrode (A). The magnification SEM image (Fig. 3b) displays that the cells (indicated by the arrow) are surrounded by ATO nanoparticles, showing the intimate association between them, which is important for electron transfer from cells to ATO nanoparticles.[45] When the concentration of the added ATO nanoparticles increased to 20 mM, the redox pair assigned to OM c-Cyts disappeared in CV (Fig. S3, solid curve), but a higher bio-catalytic current than that with the addition of 2 mM ATO nanoparticles (Fig. S3, dashed curve) can be observed. Therefore, we speculate that the *S. loihica* PV-4 cells contact directly with ATO nanoparticles that acted as microelectrodes for electron transfer from cells to the ITO electrode. Fig. S4 gives the Nyquist plots of electrochemical impedance spectroscopy (EIS) of the *S. loihica* PV-4 cells cultured on the ITO electrode in the presence (solid circle) and the absence (hollow circle) of ATO nanoparticles. It shows that the charge-transfer resistance of the composite biofilm with ATO nanoparticles is ca. 41 KΩ, which is four times lower than that of the control biofilm without ATO nanoparticles (ca. 164 KΩ), indicating the much higher EET performance of the composite biofilm. Compared with the control biofilm in the absence of ATO nanoparticles (Fig. S5a), in addition, the composite biofilm (Fig. S5b) demonstrates that ATO nanoparticles are beneficial for the formation of the biofilm that could facilitate bacterial electron transfer from microbes to electrode.

As revealed by previous study, the utilization of different EET pathways by *Shewanella* exhibits a potential-dependent behavior. Specifically, the EET pathway through direct contact via OM c-Cyts functions when the potential (E) is more positive than the redox potential of the OM c-Cyts (E_{OMC}), otherwise the EET indirectly mediated by flavins happens.[46] Accordingly, the EET should be proceeded directly through contact between microbes and electrodes via OM c-Cyts when setting

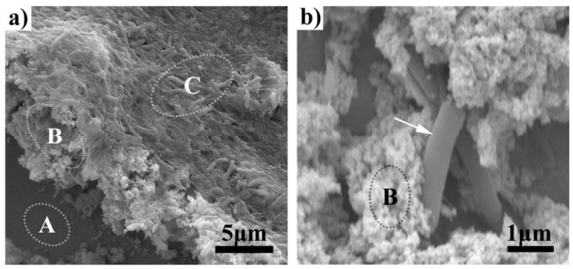

Fig. 3 (a) SEM image of the *S. loihica* PV-4 cells on the surface of the ITO electrode after 20 h of electrochemical culture at +0.2 V vs. Ag|AgCl (saturated KCl) in the presence of ATO nanoparticles; the ITO glass (A), ATO nanoparticles (B) and cells (C) were indicated by the dashed circles. (b) The enlarged SEM image of *S. loihica* PV-4 cells (indicated by the white arrow), surrounded by the ATO nanoparticles (B).

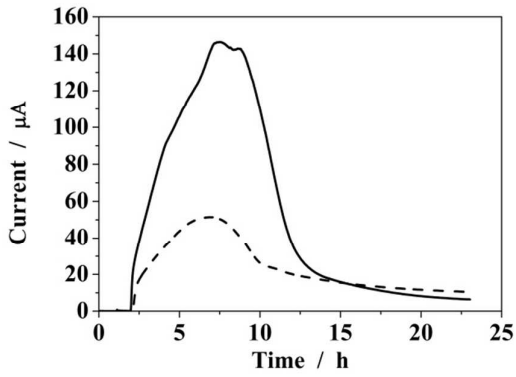

Fig. 4 Current versus time (I-t) measurements of current generation by *S. loihica* PV-4 wild type (solid curve) and its Δ2525 mutant (dashed curve) cells cultured on an ITO electrode in the presence of ATO nanoparticles.

anodic potential at +0.2 V ($E > E_{OMC}$). To probe the participation of Om c-Cyts in the microbial current generation in the presence of ATO nanoparticles, current-time (I-t) curves of *S. loihica* PV-4 wild type and Δ2525 mutant cells were measured at an potential of +0.2 V. It is known that Δ2525 mutant is lacked the decaheme c-Cyt MtrC homologue (Shew2525), which is needed for main path of EET toward electrode and current generation of *S. loihica* PV-4.[44, 47, 48] Indeed, the ability of Δ2525 mutant to transfer electron toward electrode was impaired due to the lack of MtrC, as verified by the CV curves with scan rate of 1 $mV \cdot s^{-1}$ in Fig. S6. From I-t curves in Fig. 4, it can be seen that the microbial current of Δ2525 mutant displays a 65 % decrease (dashed curve) compared with that of wild-type cells (solid curve) in the presence of ATO nanoparticles, reflecting a significant impair for current generation. We therefore conclude that the impaired ability of current generation of Δ2525 mutant in the presence of ATO nanoparticles demonstrates that the OM c-Cyts play a critical role in the electron transfer between the cells and ATO nanoparticles interface.

To investigate the activity of the EET mediated by cell-secreted flavins, we observed the effects of the current generation by adding exogenous riboflavin at the potential of +0.2 V (vs. Ag/AgCl). In the experiment, the riboflavin (6 μM) was added into the electrochemical cell after the stablization of the microbial current. Generally, *Shewanella* cells mainly utilize the EET pathway through direct contact between cells and electrode by the expression of the OM c-Cyts when the anodic potential is +0.2 V (vs. Ag/AgCl).[46] In accordance with that phenomena, the microbial current of *S. loihica* PV-4 cells barely increased after adding riboflavin into the electrochemical system in the absence of ATO nanoparticles, as given in Fig. 5a. On the contrary, the exogenous addition of

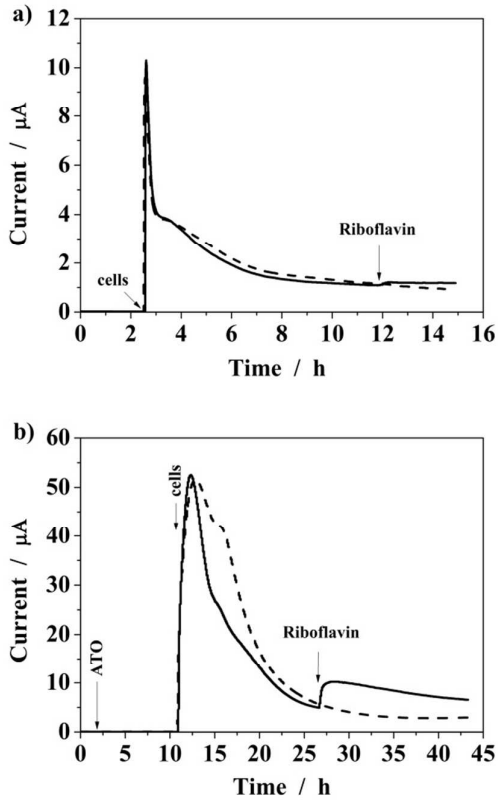

Fig. 5 (a) Time courses of microbial current by *S. loihica* PV-4 cells with (solid curve) and without (dashed curve) the addition of riboflavin indicated by the arrow in the absence of ATO nanoparticles. (b) Time courses of microbial current by *S. loihica* PV-4 cells with (solid curve) and without (dashed curve) the addition of riboflavin indicated by the arrow in the presence of ATO nanoparticles.

riboflavin resulted in an obvious increase of about 5 μA for the microbial current in the presence of ATO nanoparticles (Fig. 5b), demonstrating that the EET indirectly mediated by flavins is accelerated due to ATO nanoparticles, even though the electrode is poised at +0.2 V (vs. Ag/AgCl). We propose that the accelerated EET mediated by flavins is related to the alteration of the redox state of OM c-Cyts, as verified by the positive shift of their E_m in the presence of ATO nanoparticles, since different EET pathways are switched depending on the redox state of the OM c-Cyts.[46]

The tricarboxylic acid (TCA) cycle is one of the redox-active systems in living cells, which can provide energy for cellular growth and maintenance. It is reported that the activity of the TCA cycle in *Shewanella* cells is a potential-dependent behavior, which can be activated in potential region of -0.2 V ~ 0.1 V vs. SHE.[49] Accordingly, the TCA cycle of *S. loihica* PV-4 cells is supposed to be deactivated at +0.2 V vs. Ag/AgCl. The activity of TCA cycle in *S. loihica* PV-4 cells was investigated in the presence and the absence of ATO nanoparticles at +0.2 V (vs. Ag/AgCl) by adding malonic acid (MA), a representative

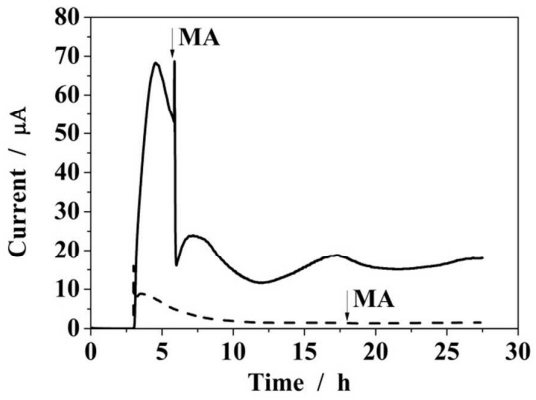

Fig. 6 I-t curves of *S. loihica* PV-4 cells before and after the addition of MA indicated by the arrow at poised potential of +0.2 V versus Ag|AgCl (sat. KCl) in the presence (solid curve) and the absence (dashed curve) of ATO nanoparticles.

inhibitor of the TCA cycle. As shown in Fig. 6, in the absence of ATO nanoparticles (dashed curve), no obvious decrease of the microbial current was observed after the injection of MA, in accordance with the reported result above.[49] In contrast, in the presence of ATO nanoparticles, the microbial current showed an immediate and drastical decrease upon adding MA, demonstrating that the TCA cycle is active even at +0.2 V (vs. Ag/AgCl). As reported previously,[41] the balance between the electron input from respiration and the output by EET could be reflected by the oxidation state of hemes in OM c-Cyts. Therefore we speculate that the active metabolism causes the change of redox state of OM c-Cyts in the presence of ATO nanoparticles, leading to an enhancement of EET process.

According to the results mentioned above, the proposed mechanism for the improved EET by ATO nanoparticles is summarized by the cartoon in Fig. 7. In the presence of ATO nanopsrticles (Fig. 7b), EET mediated by cell-secreted flavins is

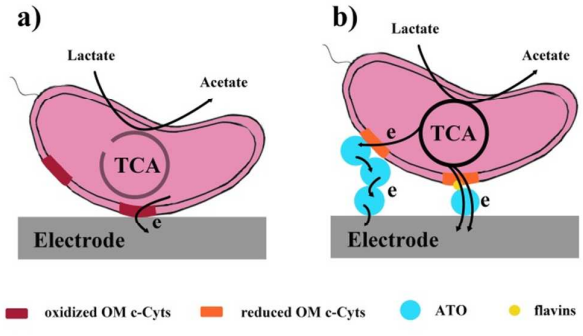

Fig. 7 Schematic illustrations for the proposed mechanism of electron transfer in the absence (a) and the presence (b) of ATO nanoparticles.

accelerated due to the reduced OM c-Cyts, and the TCA cycle is activated at the same time, thus making more electrons transfer to electrode through ATO nanoparticles. While EET is mainly proceeded via the oxidized OM c-Cyts to the electrode in the absence of ATO nanoparticles (Fig. 7a).

Conclusions

In summary, we firstly demonstrate that the microbial current of *S. loihica* PV-4 cells could be improved drastically (ca. 115-fold) by adding exogenous ATO nanoparticles that acted as active microelectrodes. It is found that the OM c-Cyts with reduced hemes are formed in the presence of ATO nanoparticles, which could adsorb cell-secreted flavins as redox cofactor with good stabilization to facilitate electron transfer. Besides, the added ATO nanoparticles are able to facilitate the formation of the composite biofilm of ATO nanoparticles and cells, benefitting the electron transfer between microbes and electrode. And the OM c-Cyts play a critical role in the direct electron transfer between the interface of cells and ATO nanoparticles. In addition, the EET mediated through flavins secreted by *S. loihica* PV-4 cells is accelerated in relation to the altering redox state of OM c-Cyts in the presence of ATO nanoparticles even if at anodic potential of +0.2 V (vs. Ag/AgCl). Moreover, the TCA cycle inside the cells is activated due to the addition of ATO nanoparticles, which could supply a continuous electron flow, resulting in the reduction of the hemes in OM c-Cyts, and then enhancing EET process. Our present findings may provide a simple and effective strategy to boost EET of *S. loihica* PV-4 cells, which is advantageous to potentially apply in bioelectrochemical systems such as MFCs and MECs.

Experimental Section

Microbe preparation

Shewanella loihic PV-4 and OM c-Cyts mutant strain (mutant Δ2525) were cultured aerobically in 10 mL Marine Broth (MB) (37.4 g · L^{-1}) and Luria-Bertani (LB) broth respectively at 30 ˚C for 18 h. Then MB/LB was replaced with 30 mL of a defined medium (DM) consisting of $NaHCO_3$ (2.5 g), $CaCl_2 \cdot 2H_2O$ (0.08 g), NH_4Cl (1.0 g), $MgCl_2 \cdot 6H_2O$ (0.2 g), NaCl (10 g), 2-[4-(2-hydroxyethyl)-1-piperazinyl] ethanesulfonic acid (HEPES, 7.2 g) per liter supplemented with (10 mM) sodium lactate (DML) as the sole carbon and energy source. The cells were further cultivated aerobically at 30 ˚C for 6 h in DML solution. Thereafter the cells were collected by centrifugation, washed two times with DML solution and finally re-suspended in DML for electrochemical measurements. The concentration of the cell suspension used for electrochemical measurements was set to be the optical density at 600 nm of 2.0.

Electrochemical measurements

A single chamber, three-electrode system was used for investigating the electrochemical behavior of intact cells of *Shewanella*. The reference electrode (RE) and counter electrode (CE) were a Ag|AgCl (sat. KCl) and a platinum wire, respectively. The ITO glass was used as the working electrode and was placed on the bottom surface of the reactor. First the electrode potential was poised at a potential of +0.2 V vs. Ag|AgCl (sat. KCl). Prior to the injection of microbial cells, ATO nanoparticles suspended in DML solution was added into the reactor and settled on the electrode surface. After that, microbial cells are injected, resulting microbial current generation along with the formation of anodic biofilms. The cyclic voltammogram (CV) and differential pulse voltammogram (DPV) were measured using a CHI 1030B electrochemical workstation (CH Instruments, USA). DML (4 mL) solution was used as the electrolyte and was deaerated by N_2 bubbling for 10 min before measurements. Temperature of the system was kept at 30 ˚C. No agitation was made during the measurements.

Acknowledgements

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