November 1, 2012

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Energy & Environmental Science

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Cite this: *Energy Environ. Sci.*, 2013, **6**, 217

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Microbial electrosynthesis is a promising strategy for the microbial conversion of carbon dioxide to transportation fuels and other organic commodities, but optimization of this process is required for commercialization. Cathodes which enhance electrode–microbe electron transfer might improve rates of product formation. To evaluate this possibility, biofilms of *Sporomusa ovata*, which are effective in acetate electrosynthesis, were grown on a range of cathode materials and acetate production was monitored over time. Modifications of carbon cloth that resulted in a positive-charge enhanced microbial electrosynthesis. Functionalization with chitosan or cyanuric chloride increased acetate production rates 6–7 fold and modification with 3-aminopropyltriethoxysilane gave rates 3-fold higher than untreated controls. A 3-fold increase in electrosynthesis over untreated carbon cloth cathodes was also achieved with polyaniline cathodes. However, not all strategies to provide positively charged surfaces were successful, as treatment of carbon cloth with melamine or ammonia gas did not stimulate acetate electrosynthesis. Treating carbon cloth with metal, in particular gold, palladium, or nickel nanoparticles, also promoted electrosynthesis, yielding electrosynthesis rates that were 6-, 4.7- or 4.5-fold faster than the untreated control, respectively. Cathodes comprised of cotton or polyester fabric treated with carbon nanotubes yielded cathodes that supported acetate electrosynthesis rates that were ~3-fold higher than carbon cloth controls. Recovery of electrons consumed in acetate was ~80% for all materials. The results demonstrate that one approach to increase rates of carbon dioxide reduction in microbial electrosynthesis is to modify cathode surfaces to improve microbe-electrode interactions.

Received 3rd September 2012
Accepted 1st November 2012

DOI: 10.1039/c2ee23350a

www.rsc.org/ees

Broader context

Microbial electrosynthesis is a recently conceived bioenergy strategy in which microorganisms use electrons derived from electrodes to reduce carbon dioxide to organic products that are excreted from the cells. Any form of electrical energy can power microbial electrosynthesis, but when electricity is obtained from solar technologies and water is the source of electrons, microbial electrosynthesis is an artificial form of photosynthesis with many potential advantages over biomass-based energy strategies. This study demonstrates that there are several strategies for modifying cathode surface properties that can enhance rates of microbial electrosynthesis.

Introduction

Microbial electrosynthesis is a novel bioenergy strategy in which electricity serves as the energy source for microbial reduction of carbon dioxide to multi-carbon organic molecules that can serve as transportation fuels or other useful organic commodities.[1–4] The conversion of electrical energy to extracellular, multi-carbon products represents an attractive option for energy storage and distribution.[5] When the electricity for microbial electrosynthesis is derived from solar sources, microbial electrosynthesis represents an artificial form of photosynthesis with many potential advantages over bioenergy strategies that rely on biological photosynthesis.[3,4,6–8] Initial proof-of-concept studies demonstrated that acetogenic bacteria, such as *Sporomusa* and *Clostridium* species, could accept electrons from negatively charged graphite electrodes as the electron donor for the reduction of carbon dioxide to acetate that was released extracellularly.[3,4] *Clostridium ljungdahlii*, one of the strains capable of electrosynthesis, can be genetically manipulated,[9] offering the promise of generating products with higher value than acetate.[3]

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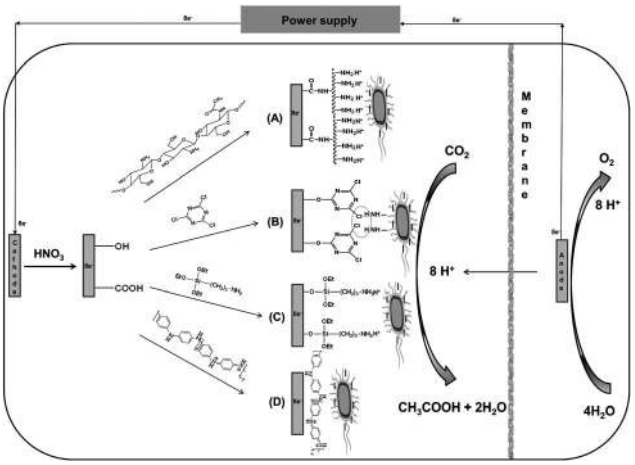

Scheme 1 Schematic of the cathode configuration and electron-consumption between *S. ovata* and electrode for the electrosynthesis of acetate. (A) Carbon cloth cathode coated by chitosan. (B) Carbon cloth cathode coated with cyanuric chloride. (C) Carbon cloth cathode coated with 3-aminopropyltriethoxysilane. (D) Carbon cloth cathode coated with PANi.

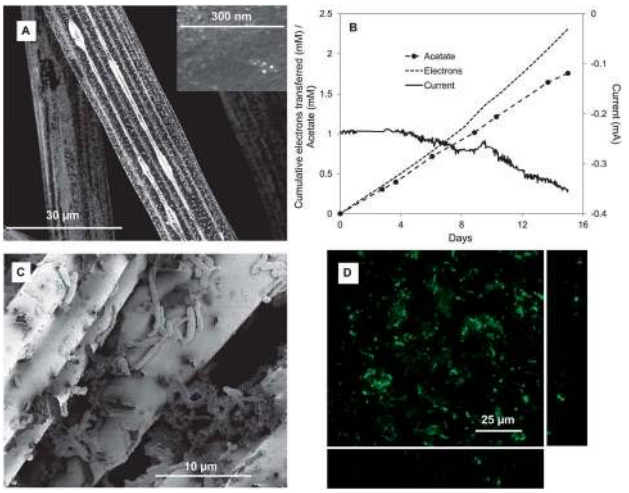

Fig. 1 *S. ovata* electrosynthesis of acetate with untreated carbon cloth cathode. (A) SEM image of the untreated carbon cloth. (B) Electron consumption, acetate and current production over time (C) SEM image of *S. ovata* on the cathode. (D) Confocal scanning laser microscopic image of *S. ovata* on the cathode. Results shown are from a representative example of three replicate cultures.

Commercialization of microbial electrosynthesis will require optimization and scaling. One key feature is enhancing electron exchange at the cathode surface while maintaining low costs. Although there have been substantial improvements in understanding how microorganisms transfer electrons to electrodes, the mechanisms for electron transfer from electrodes to microbes are still poorly understood.[1,2,8,10,11] Thus, initial approaches to improve cathode design are likely to be largely empirical, but still potentially productive. For example, cathode-driven anaerobic respiration by *Geobacter sulfurreducens*[12] was enhanced by switching from graphite to different forms of stainless steel and modifying surface roughness.[13–15]

A number of approaches that can improve microbe–electrode electron exchange (Scheme 1) have been identified in studies of anode material studies for biosensors and microbial fuel cells.[16–22] For example, a positive charge at the electrode surface, established with ammonia gas treatment,[23] chitosan,[24–29] cyanuric chloride (CC),[30–33] 3-aminopropyltriethoxysilane (APTES),[34–37] melamine[38,39] or polyaniline (PANi),[40–46] has the potential of leading to better electron transfer. Thin layers of metal catalysts, such as Au,[17,47–50] Pd[17,47,50–52] or Ni,[17,53–56] can reduce the activation energy threshold of electron transfer from electrodes to bacteria. Fabrics coated with carbon nanotubes offer an open, three-dimensional, conductive matrix for microbial growth.[57–61]

Here, we report on a study of the performance of diversity of cathode materials for microbial electrosynthesis by *Sporomusa ovata.* These results suggest that several modifications that provide a positive charge at the cathode surface can effectively enhance microbial electrosynthesis rates.

Results and discussion

Carbon cloth was a suitable cathode material for microbial electrosynthesis with *Sporomusa ovata* (Fig. 1 and Table 1). There was a steady consumption of current over time with the concomitant production of acetate (Fig. 1B). Recovery of electrons consumed in acetate was high (74 ± 14%; mean ± standard deviation, $n = 3$). Acetate production could be attributed to cells attached to the cloth fibers (Fig. 1C) which live/dead staining indicated were metabolically active (Fig. 1D).

Cathode modifications to confer positive surface charge

Gram negative microorganisms like *S. ovata* typically have a negative outer-surface charge.[62,63] The surface charge of untreated carbon cloth is neutral.[64] Therefore, strategies for generating a positively charged cathode surface were evaluated to determine if this approach would promote better electronic interaction between the cells and the cathode.

Chitosan, an amino- and hydroxyl-group rich polysaccharide, is one of the most commonly used natural biopolymers for enzyme immobilization[65,66] or the dispersion of

Table 1 The average current consumption density and acetate production rate of electrosynthesis

Carbon cloth cathode treatment	Average current consumption density[a] (mA m^{-2})	Acetate[a] (mM m^{-2} day^{-1})	Coulombic efficiency[a]
Carbon cloth	−71 ± 11	30 ± 7	76 ± 14
Chitosan	−475 ± 18	229 ± 56	86 ± 12
Cyanuric chloride	−451 ± 79	205 ± 50	81 ± 16
3-Aminopropyltriethoxysilane	−206 ± 11	95 ± 20	82 ± 11
Polyaniline	−189 ± 18	90 ± 22	85 ± 7
Melamine	−69 ± 9	31 ± 8	80 ± 15
Ammonia	−60 ± 21	28 ± 14	82 ± 8
Au	−388 ± 43	181 ± 44	83 ± 14
Pd	−320 ± 64	141 ± 35	79 ± 16
Ni	−302 ± 48	136 ± 33	80 ± 15
CNT–cotton	−220 ± 1	102 ± 25	83 ± 10
CNT–polyester	−210 ± 13	96 ± 24	82 ± 8

[a] Each value is the mean and standard deviation of three replicates.

nanoparticles[67] in biosensors or microbial fuel cells[27,28] due to its biocompatibility, nontoxicity, film-forming ability, high water permeability, excellent mechanical strength and low cost.[26,29] Chitosan was bound to the carbon cloth *via* the reaction between –COOH groups on the electrode surface and $–NH_2$ groups on the chitosan (Scheme 1A). Scanning electron microscopy revealed that a thin layer of chitosan covered the entire electrode surface, with pore sizes suitable for microbial access (Fig. 2A). The rate of acetate production *via* microbial electrosynthesis (Fig. 2B and Table 1) was 7.6-fold higher than with the unmodified carbon cloth electrode (Fig. 1B). Electron recovery in acetate remained high with 86% ± 12% of the electrons consumed recovered in acetate (Fig. 2B). Confocal laser-scanning fluorescence microscopy (Fig. 2C) revealed a more than 9-fold higher cell density on the chitosan modified cathode $3.02 \pm 1.95 \times 10^7$ cells per cm^{-2} than the untreated cloth $3.98 \pm 1.24 \times 10^6$ cells per cm^{-2}, which may account for the higher rates of electrosynthesis.

Cyanuric chloride (2,4,6-trichloro-1,3,5-triazine) has been widely used to modify graphite electrodes to promote the attachment of enzymes.[30–33] In addition to providing an overall positive charge, there is the possibility that chlorines that have

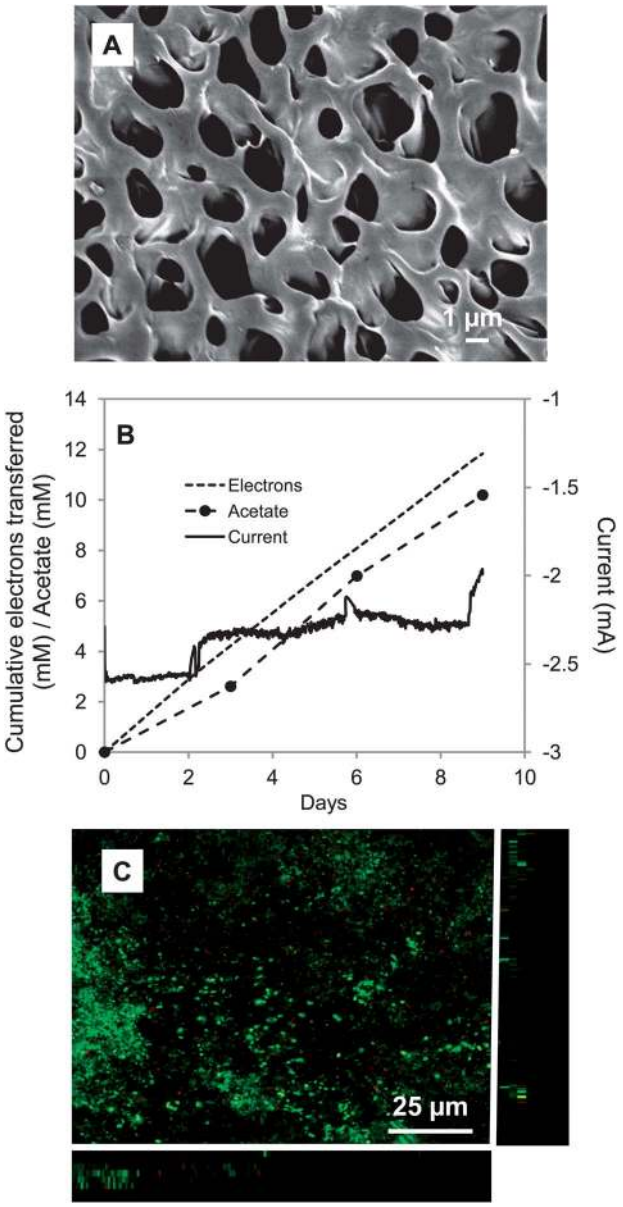

Fig. 2 *S. ovata* electrosynthesis of acetate with chitosan-coated carbon cloth cathode. (A) SEM image of the chitosan-coated carbon cloth. (B) Electron consumption, acetate and current production over time. (C) Confocal scanning laser microscopic image of *S. ovata* on the cathode. Results shown are from a representative example of three replicate cultures.

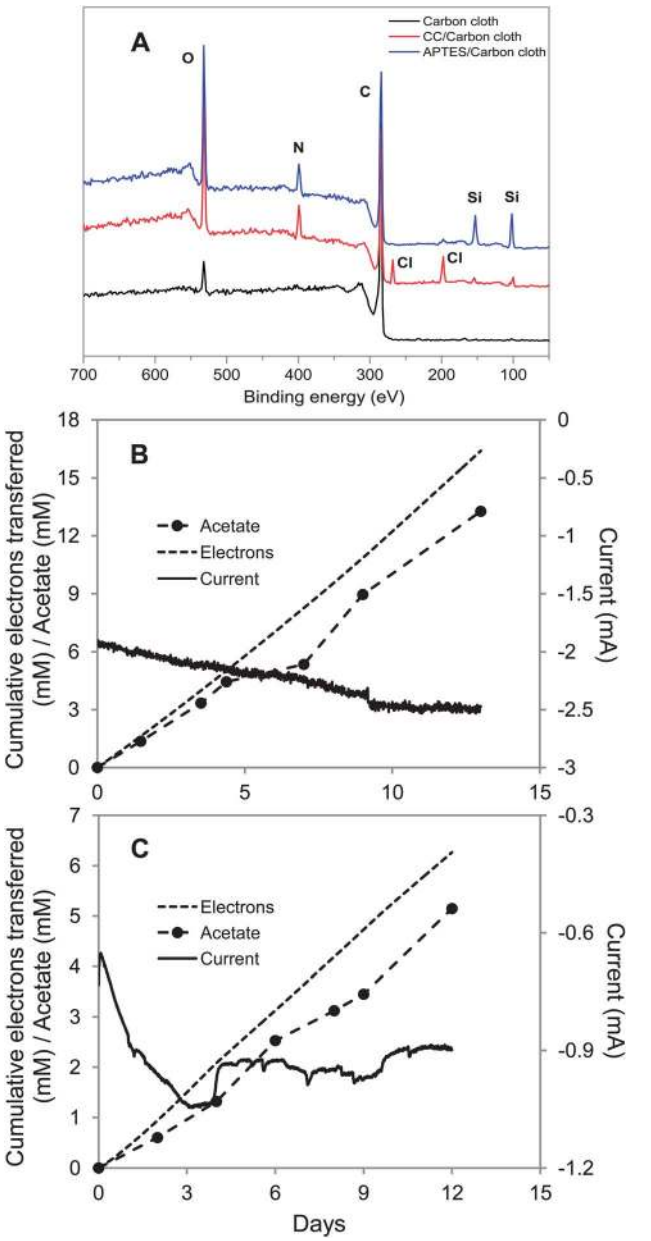

Fig. 3 *S. ovata* electrosynthesis of acetate with carbon cloth cathodes coated with cyanuric chloride or 3-aminopropyltriethoxysilane. (A) XPS spectra untreated and treated carbon cloth. (B) Electron consumption, acetate and current production over time with the cyanuric chloride-coated carbon cloth. (C) Electron consumption, acetate and current production over time with the 3-aminopropyltriethoxysilane-coated carbon cloth. Results shown are from a representative example of three replicate cultures.

not reacted with the carbon cloth will react with functional groups on the cell surface, such as amino groups of surface-exposed proteins, to promote absorption of bacteria onto the electrode surface.[68] X-ray photoelectron spectroscopy confirmed the binding of cyanuric chloride to carbon cloth (Fig. 3A). Edges corresponding to N 1s (binding energy, 400 eV), Cl 2s (binding energy, 269.6 eV) and Cl 2p (binding energy, 197.6 eV) were apparent in the profiles of the cyanuric chloride-modified carbon cloth, whereas only carbon and oxygen edges, corresponding to C 1s (binding energy, 284.6 eV) and O 1s (binding energy. 532 eV), were observed in the spectrum of the untreated carbon cloth (Fig. 3A). The rate of acetate production *via* electrosynthesis with the cyanuric chloride-treated cloth was 6.8-fold higher than for untreated cloth with a recovery of 81% ± 16% ($n = 3$) of the electrons consumed recovered in acetate (Fig. 3B and Table 1).

3-Aminopropyltriethoxysilane (APTES) is commonly used for surface functionalization in biosensors because the silane group can covalently bind to the silicon oxide substrate and amine functionality can promote the adsorption of negatively charged proteins or other biomolecules.[34–36,69] Hydroxyl groups exposed on the surface of HNO_3-pretreated carbon cloth electrode are expected to covalently bind APTES to the electrode surface (Scheme 1C). Evidence for the attachment of APTES to the carbon cloth was provided by the appearance of two edges at 192.8 and 101.6 eV arising from the Si 2s and Si 2p, as well as N 1s edge (400 eV), in the XPS spectra after surface modification (Fig. 3A). Acetate electrosynthesis rates were 3-fold higher than those with the untreated carbon cloth (Fig. 3C and Table 1) with a recovery of electrons consumed in acetate of 82% ± 11%.

Polyaniline (PANi), an organic conducting polymer, has been used to modify anodes in microbial fuel cells to improve performance, due to its high electrical conductivity, ease of synthesis, and chemical stability.[40,41,43] Electrospinning is a straightforward technique for fabricating three-dimensional scaffolds with high surface to volume ratios, significant fiber interconnectivity, and microscale porosity.[45,70,71] Polymer fibers, obtained by using the electrospinning technique, afford a nanofibrous scaffold with strong adsorbability and abundant space for biomacromolecules.[70] PANi–PAN was prepared by electrospinning with coaxial polymer nanofibers of PANi and polyacrylonitrile (PAN). Microporous composite mats of PANi–PAN were obtained (Fig. 4A). The rate of acetate production with PANi–PAN cathodes was 3-fold higher than for the control carbon cloth (Fig. 4B and Table 1) with a recovery of electrons consumed in acetate production of 85% ± 7%.

In contrast to the enhancement in acetate electrosynthesis with the cathode modifications summarized above, two other modifications designed to generate a positively charged cathode surface were not successful. Treating carbon cloth with melamine or ammonia is expected to yield a positive surface charge due to the presence of nitrogen-containing surface functional groups.[23,72] However, neither of these treatments enhanced microbial electrosynthesis of acetate over that in untreated controls.

These results demonstrated that it is possible to enhance the rate of microbial electrosynthesis by modifications that provide a positive charge at the cathode surface. However, a positive charge is not sufficient and other features of the cathode modifications designed to provide a positive charge may be important.

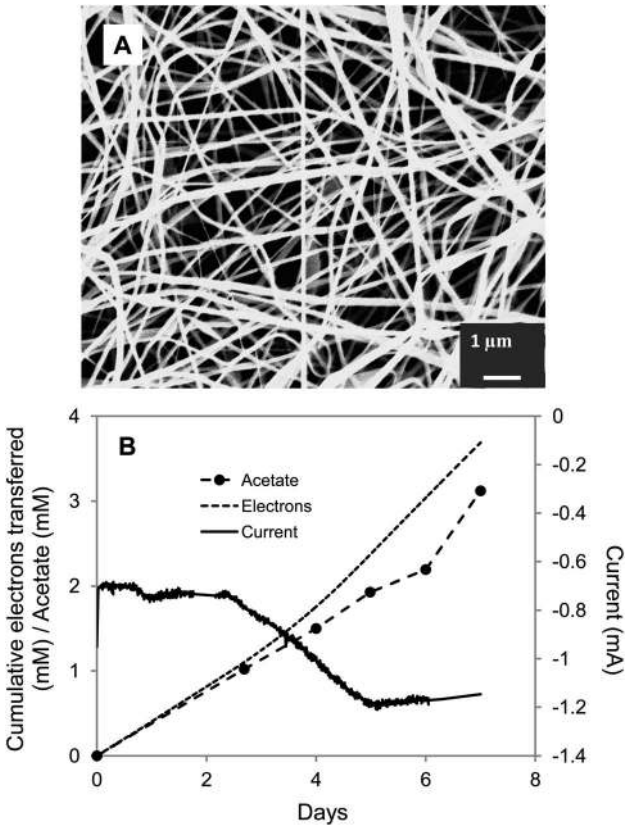

Fig. 4 *S. ovata* electrosynthesis of acetate with carbon cloth cathode coated with PANi–PAN. (A) SEM image of the PANi–PAN coated carbon cloth. (B) Electron consumption, acetate and current production over time. Results shown are from a representative example of three replicate cultures.

Cathode modification with metal nanoparticles

Metal nanoparticles are attractive possibilities for enhancing electrode–microbe electron exchange because they have excellent catalytic activity, biocompatibility, high active surface area, and chemical stability, and their particle sizes can readily be controlled.[50,53] Enhanced performance of biosensors and microbial fuel cells has been achieved with metal nanoparticles,[17,47,54] which can facilitate electron transfer between the cells and electrode due to the low charge-transfer resistances and high conductivities of the nanoparticles.[50,52]

In order to evaluate their potential for improving electrosynthesis, thin layers of Au, Pd or Ni nanoparticles were homogeneously coated onto the carbon cloth by physical deposition. Characteristic (111) X-ray diffraction (XRD) peaks of Au, Pd, or Ni were observed at 38.4°, 40.2° or 45.2°, respectively, confirming nanoparticles deposition (Fig. 5A). Each of the treatments promoted acetate electrosynthesis with rates 6-, 4.7- or 4.5-fold faster than the untreated control for Au, Pd, and Ni, respectively (Fig. 5B–D and Table 1). In each case electron recovery in acetate was comparable to other cathode modification strategies.

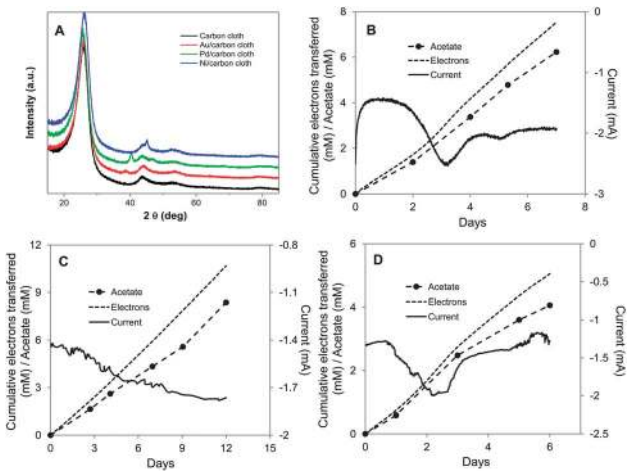

Fig. 5 *S. ovata* electrosynthesis of acetate with carbon cloth cathodes coated with metal nanoparticles. (A) X-ray diffraction patterns of plain carbon cloth or cloth coated with Au, Pd, or Ni nanoparticles. (B) Electron consumption, acetate and current production over time with Au nanoparticle coated carbon cloth. (C) Electron consumption, acetate and current production over time with Pd nanoparticle coated carbon cloth. (D) Electron consumption, acetate and current production over time with Ni nanoparticle coated carbon cloth. Results shown are from a representative example of three replicate cultures.

Carbon nanotube–textile composite cathode

Electrodes modified with carbon nanotubes (CNTs) have been shown to enhance the performance of biosensing systems[61,73–75] and microbial fuel cells,[57,58,60] due to their high aspect ratio, high conductivity and excellent biocompatibility. It is possible to incorporate CNTs into lightweight, stretchable and flexible textiles, like cotton[58,76,77] or polyester fabric[77] by a simple, yet scalable, dip-coating process. Polyester or carbon fabric were successfully coated with single-walled carbon nanotubes (SWNTs) as described in the literature,[58] with stronger and more efficient adsorption on polyester or cotton sheets than on carbon fiber, as reported previously.[76] After 8 repetitive dipping and drying steps, the polyester and cotton fabric became conductive with a low resistivity of 50 Ω cm^{-1}. The SWNTs were well-distributed on the cotton (Fig. 6A) and polyester textile fibers (Fig. 6D) and cells readily attached to the materials (Fig. 6C and F). The rate of acetate production by *S. ovata* was comparable with both materials with rates that were 3.4- and 3.2-fold higher than the control (Fig. 6B and E and Table 1). Electron recoveries were comparable with other materials.

Experimental

Organism source and culture conditions

Sporomusa ovata (DSM 2662) was obtained from Deutsche Sammlung Mikroorganismen und Zellkulturen and routinely grown in DSM medium 311 (omitting betaine, fructose, casitone, and resazurin) with hydrogen as the electron donor (H_2–CO_2 [80 : 20]) at 30 °C under strict anaerobic conditions as previously described.[3,4,78]

Chemicals

Chitosan, cyanuric chloride (CC, 2,4,6-trichloro-1,3,5-triazine), 3-aminopropyltriethoxysilane (APTES), polyacrylonitrile (PAN, M_w, 150k), polyaniline (PANi, emeraldine base, M_w, 6.4k),

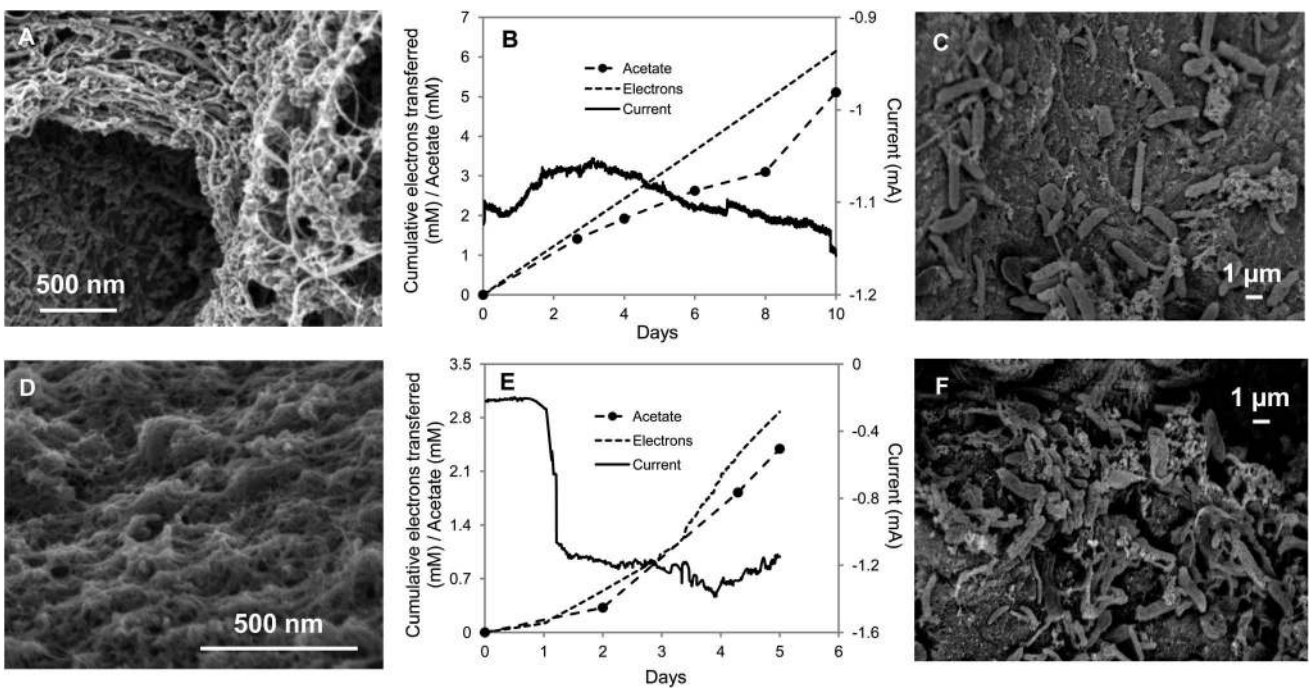

Fig. 6 *S. ovata* electrosynthesis of acetate with carbon nanotube–textile composite. (A) SEM image of the cotton fabric coated with carbon nanotubes (CNTs). (B) Electron consumption, acetate and current production over time with CNT–cotton cathode. (C) SEM image of *S. ovata* on the CNT–cotton. (D) SEM image of the CNT–polyester. (E) Electron consumption, acetate and current production over time with CNT–polyester cathode. (F) SEM image of *S. ovata* on the CNT–polyester. Results shown are from a representative example of three replicate cultures.

N-hydroxysuccinimide melamine, 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide, camphor-10-sulfonic acid and single-walled carbon nanotubes (SWNTs) were purchased from Sigma-Aldrich.

Acetate production by microbial electrosynthesis with an electrode as the electron donor

Each cathode material was tested at 25 °C in a three-electrode, dual-chambered system, with *S. ovata* grown in the cathode chamber as described previously.[3,4] The carbon cloth cathode (47 cm^2; GC-14, Electrolytica, Amherst, NY) and graphite stick anode (65 cm^2; Mersen, Greenville, MI) were suspended in 200 ml of media in two chambers which are separated by a Nafion 117 cation-exchange membrane (Electrolytica, Amherst, NY). The anode chamber was continually bubbled with N_2–CO_2 (80 : 20). The cathode was equipped with a potentiostat (ECM8, Gamry Instruments, PA, USA) at −600 mV (*versus* Ag/AgCl). Hydrogen-grown cultures of *S. ovata* were established in the cathode chamber with a hydrogen-containing gas mix N_2–CO_2–H_2 (83 : 10 : 7). The cathode gas mix was switched to N_2–CO_2 (80 : 20) after several fresh medium swaps. As previously described,[4] there was no significant H_2 production with any of the cathode materials and although some of the cathode materials were organic, they did not serve as a carbon source for acetate production as evidenced by a lack of acetate production when cathodes were not connected to anodes, as well as the correspondence between electron consumption and electrons appearing in products during electrosynthesis.

Electrode modification procedure

Positively charged surface modification. The carbon cloth was pretreated with concentrated HNO_3 overnight, then thoroughly washed with milli-Q water (18.2 MΩ cm) and dried with nitrogen gas, before the electrode surfaces were covalently modified with chitosan, cyanuric chloride, 3-aminopropyltriethoxysilane, or melamine. Chitosan coating was prepared by drop casting 2 ml of 2% chitosan aqueous solution onto the carbon cloth. Then the dried electrodes were immersed in ethanol–water (4 : 1, v/v) coupling medium containing 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide and *N*-hydroxysuccinimide (50 mM/50 mM) at room temperature overnight, then carefully washed with ethanol and dried by vacuum at room temperature overnight. Cyanuric chloride was anchored onto the electrode surface by immersing carbon cloth in 50 mM cyanuric chloride toluene solution for 24 h as previously described.[32] To improve the density of cyanuric chloride on the electrode surface, the reaction was performed at 0 °C rather than room temperature. 3-Aminopropyltriethoxysilane functionalized electrode surface were obtained by immersing HNO_3-pretreated carbon cloth in a 5% 3-aminopropyltriethoxysilane solution in an anhydrous toluene for 30 min. After carefully washing with toluene and acetone to remove the non-specific 3-aminopropyltriethoxysilane, the carbon cloth electrodes were dried at 110 °C for 1 h. Melamine treated electrodes were obtained by immersion of carbon cloth in methanol–water solution (1 : 1, v/v) containing 50 mM of melamine, 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide and *N*-hydroxysuccinimide (50 mM/50 mM) at room temperature overnight. Then they were washed with methanol several times to remove the unabsorbed melamine.

Carbon cloth was ammonia-treated with a gas mix of 5% NH_3 and 95% helium as previously described.[23]

Electrospun mats of PANi–PAN

Nanofibrous mats of PANi–PAN were fabricated by electrospinning as previously described.[79] 2% of PANi solution was obtained by doping PANi base with camphor-10-sulfonic acid, filtered, and then washed with dimethylformamide. By dissolving PAN in the 2% of PANi solution, polymer solution was obtained and used for electrospinning at 25 kV. The feeding rate was 20 μl min^{-1} and the collecting distance was 15 cm. The composite fibers were collected on the carbon cloth. The electrospinning apparatus included a high voltage power supply (AU-120P0.5, Matsusada Precision Inc., Kusatsu, Shiga, Japan), a syringe pump (KDS 101, KD Scientific Inc., Holliston, MA) and a grounded cylinder target.

Deposition of metal nanoparticles

Au and Ni layers were homogeneously sputtered on the carbon cloth for 100 s. The thin Pd layer was obtained through vapor-deposition.

Carbon nanotube–textile composite

Carbon nanotube–textile composite electrode was synthesized through a simple process by dipping–drying textile cloth in aqueous CNT ink, which was prepared by dispersing 0.16% of single-walled CNTs in water by weight and 1% of sodium dodecylbenzene sulfonate as a surfactant as previously described.[58] Two types of textile were used in this procedure, a piece of intertwined polyester fiber (1 mm in thickness) and a cotton sheet (1–2 mm in thickness) from JoAnn Fabric.

Analytical methods

Acetate was measured *via* high performance liquid chromatography (HPLC) as previously described.[3,80] The biofilms of *S. ovata* on the cathodes were stained with the LIVE/DEAD BacLight Viability Kit and imaged with confocal laser microscopy as previously described.[3,80] The average cell number was calculated by examining at least five fields of view. For examination with scanning electron microscopy (SEM), samples of cathode materials were collected and fixed overnight in a buffer solution (0.1 M phosphate buffer, pH 7) containing 2.5% glutaraldehyde at room temperature. Then, samples were washed using a phosphate buffer solution (pH 7) and immersed successively in different aqueous solutions with increasing ethanol content (30, 50, 60, 70, 80, 90 and 100% ethanol), and was washed a second time with increasing acetonitrile content (50, 60, 70, 80, 90 and 100% acetonitrile). Vacuum dried samples were finally coated with Au before SEM observation. The microscopic features of the samples were investigated using a JEOL 6320 model scanning electron microscope (SEM) at an accelerating voltage of 5 kV.

X-ray photoelectron spectroscopy (XPS) was performed on a Physical Electronics Quantum 2000 Scanning ESCA Microprobe. Depth profiling was done by collecting spectra at 15° and 75° take-off angles with respect to the plane of the sample surface. The analysis at 15° has a penetration depth of ~10 Å and that at 75° corresponds to a penetration depth of ~40 Å.

X-ray diffraction (XRD) experiments were performed in a Shimadzu XRD-6000 X-ray powder diffractometer with Cu Kα ($\lambda = 0.154$ nm) radiation at a generator voltage of 40 kV and a current of 40 mA.

Conclusions

These results demonstrate that there are several surface modifications of cathodes that can significantly increase the rate of microbial electrosynthesis. Modifying carbon cloth with chitosan or cyanuric chloride, which is relatively inexpensive, increased microbial electrosynthesis of acetate 6–7 fold. Modification with metal nanoparticles moderately increased microbial electrosynthesis rates, and although nickel is relatively inexpensive, the cost of gold or palladium would make large-scale microbial electrosynthesis reactors with such cathodes economically infeasible.[17,81] The carbon nanotube–textile composite cathodes are the least cost effective materials due to the high cost of carbon nanotubes[81,82] with only 3-fold increase in rates of microbial electrosynthesis compared to the untreated control.

One factor limiting the design of cathode materials is a lack of understanding of the mechanisms by which electrons are transferred from cathodes to cells.[6,10,11] Rates of microbial electron transfer to anodes as high as 30 A m^{-2} have been reported[22] and cathode biofilms of *Geobacter sulfurreducens* consumed up to 20 A m^{-2} when reducing fumarate.[83] If similar rates of electron transfer could be achieved with microorganisms reducing carbon dioxide then rates of microbial electrosynthesis could be increased 40–60 fold higher than the highest rates reported here. Preliminary mechanistic studies have been conducted on electron transfer into cells of fumarate-reducing *Geobacter sulfurreducens*,[84] but even in this instance the cell components required for cell–cathode electrical connections have not be definitively identified and *G. sulfurreducens* does not effectively reduce carbon dioxide to organic products. Further research in this area is expected to make it possible to tune materials and cathode potentials to best interact with the appropriate electron carriers in microorganisms capable of electrosynthesis and further optimize this process.

Acknowledgements

This research was supported by Advanced Research Projects Agency – Energy (ARPA-E), U.S. Department of Energy, under Award Number DE-AR0000159 to DRL and the U.S. Department of Energy, Office of Basic Energy Sciences under contract DOE-DE-FG02-45612 to TPR.

References

1 D. R. Lovley, *Energy Environ. Sci.*, 2011, **4**, 4896–4906.
2 D. R. Lovley, *Annu. Rev. Microbiol.*, 2012, **66**, 391–409.
3 K. P. Nevin, S. A. Hensley, A. E. Franks, Z. M. Summers, J. Ou, T. L. Woodard, O. L. Snoeyenbos-West and D. R. Lovley, *Appl. Environ. Microbiol.*, 2011, **77**, 2882–2886.
4 K. P. Nevin, T. L. Woodard, A. E. Franks, Z. M. Summers and D. R. Lovley, *mBio*, 2010, **1**, e00103.
5 N. S. Lewis and D. G. Nocera, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 15729–15735.
6 D. R. Lovley, *Environ. Microbiol. Rep.*, 2011, **3**, 27–35.
7 D. R. Lovley and K. P. Nevin, *Curr. Opin. Biotechnol.*, 2011, **22**, 441–448.
8 K. Rabaey and R. A. Rozendal, *Nat. Rev. Microbiol.*, 2010, **8**, 706–716.
9 M. Köpke, C. Held, S. Hujer, H. Liesegang, A. Wiezer, A. Wollherr, A. Ehrenreich, W. Liebl, G. Gottschalk and P. Durre, *Proc. Natl. Acad. Sci. U. S. A.*, 2010, **107**, 13087–13092.
10 L. Huang, J. M. Regan and X. Quan, *Bioresour. Technol.*, 2011, **102**, 316–323.
11 M. Rosenbaum, F. Aulenta, M. Villano and L. T. Angenent, *Bioresour. Technol.*, 2011, **102**, 324–333.
12 K. B. Gregory, D. R. Bond and D. R. Lovley, *Environ. Microbiol.*, 2004, **6**, 596–604.
13 C. Dumas, A. Mollica, D. Feron, R. Basseguy, L. Etcheverry and A. Bergel, *Electrochim. Acta*, 2007, **53**, 468–473.
14 L. Pons, M. L. Delia, R. Basseguy and A. Bergel, *Electrochim. Acta*, 2011, **56**, 2682–2688.
15 L. Pons, M. L. Delia and A. Bergel, *Bioresour. Technol.*, 2011, **102**, 2678–2683.
16 T. Nöll and G. Nöll, *Chem. Soc. Rev.*, 2011, **40**, 3564–3576.
17 J. Wei, P. Liang and X. Huang, *Bioresour. Technol.*, 2011, **102**, 9335–9344.
18 K. Watanabe, *J. Biosci. Bioeng.*, 2008, **106**, 528–536.
19 B. Willner, E. Katz and I. Willner, *Curr. Opin. Biotechnol.*, 2006, **17**, 589–596.
20 B. E. Logan, *Appl. Microbiol. Biotechnol.*, 2010, **85**, 1665–1671.
21 Z. Du, H. Li and T. Gu, *Biotechnol. Adv.*, 2007, **25**, 464–482.
22 S. L. Chen, H. Q. Hou, F. Harnisch, S. A. Patil, A. A. Carmona-Martinez, S. Agarwal, Y. Y. Zhang, S. Sinha-Ray, A. L. Yarin, A. Greiner and U. Schroder, *Energy Environ. Sci.*, 2011, **4**, 1417–1421.
23 S. A. Cheng and B. E. Logan, *Electrochem. Commun.*, 2007, **9**, 492–496.
24 M. N. V. R. Kumar, *React. Funct. Polym.*, 2000, **46**, 1–27.
25 V. K. Mourya and N. N. Inamdar, *React. Funct. Polym.*, 2008, **68**, 1013–1051.
26 I. T. Cavalcanti, B. V. Silva, N. G. Peres, P. Moura, M. D. Sotomayor, M. I. Guedes and R. F. Dutra, *Talanta*, 2012, **91**, 41–46.
27 S. R. Higgins, D. Foerster, A. Cheung, C. Lau, O. Bretschger, S. D. Minteer, K. Nealson, P. Atanassov and M. J. Cooney, *Enzyme Microb. Technol.*, 2011, **48**, 458–465.
28 X. W. Liu, X. F. Sun, Y. X. Huang, G. P. Sheng, S. G. Wang and H. Q. Yu, *Energy Environ. Sci.*, 2011, **4**, 1422–1427.

29 F. Kuralay, T. Vural, C. Bayram, E. B. Denkbas and S. Abaci, *Colloids Surf., B*, 2011, **87**, 18–22.
30 G. Blotny, *Tetrahedron*, 2006, **62**, 9507–9522.
31 A. C. Franzoi, I. C. Vieira, J. Dupont, C. W. Scheeren and L. F. de Oliveira, *Analyst*, 2009, **134**, 2320–2328.
32 Y. Wang and Y. Hasebe, *Sens. Actuators, A*, 2011, **155**, 722–729.
33 D. Quan and W. S. Shin, *Mater. Sci. Eng., C*, 2004, **24**, 113–115.
34 H. Li, J. Zhang, X. Zhou, G. Lu, Z. Yin, G. Li, T. Wu, F. Boey, S. S. Venkatraman and H. Zhang, *Langmuir*, 2010, **26**, 5603–5609.
35 J. J. Lin, P. Y. Hsu, Y. L. Wu and J. J. Jhuang, *Sensors*, 2011, **11**, 2796–2808.
36 V. K. S. Hsiao, J. R. Waldeisen, Y. B. Zheng, P. F. Lloyd, T. J. Bunning and T. J. Huang, *J. Mater. Chem.*, 2007, **17**, 4896–4901.
37 Y. Wang, W. Qian, Y. Tan and S. Ding, *Biosens. Bioelectron.*, 2008, **23**, 1166–1170.
38 A. Pietrzyk, W. Kutner, R. Chitta, M. E. Zandler, F. D'Souza, F. Sannicolo and P. R. Mussini, *Anal. Chem.*, 2009, **81**, 10061–10070.
39 Z. H. Sheng, X. Q. Zheng, J. Y. Xu, W. J. Bao, F. B. Wang and X. H. Xia, *Biosens. Bioelectron.*, 2012, **34**, 125–131.
40 B. Lai, X. Tang, H. Li, Z. Du, X. Liu and Q. Zhang, *Biosens. Bioelectron.*, 2011, **28**, 373–377.
41 Y. Qiao, S. J. Bao, C. M. Li, X. Q. Cui, Z. S. Lu and J. Guo, *ACS Nano*, 2008, **2**, 113–119.
42 Y. Qiao, C. M. Li, S. J. Bao and Q. L. Bao, *J. Power Sources*, 2007, **170**, 79–84.
43 K. Gurunathan, A. V. Murugan, R. Marimuthu, U. P. Mulik and D. P. Amalnerkar, *Mater. Chem. Phys.*, 1999, **61**, 173–191.
44 K. Scott, G. A. Rimbu, K. P. Katuri, K. K. Prasad and I. M. Head, *Process Saf. Environ. Prot.*, 2007, **85**, 481–488.
45 H. Antaya, M. Richard-Lacroix and C. Pellerin, *Macromolecules*, 2010, **43**, 4986–4990.
46 J. Niessen, F. Harnisch, M. Rosenbaum, U. Schroder and F. Scholz, *Electrochem. Commun.*, 2006, **8**, 869–873.
47 Y. Fan, S. Xu, R. Schaller, J. Jiao, F. Chaplen and H. Liu, *Biosens. Bioelectron.*, 2010, **26**, 1908–1912.
48 D. Brondani, E. Zapp, I. C. Vieira, J. Dupont and C. W. Scheeren, *Analyst*, 2011, **136**, 2495–2505.
49 B. K. Jena, S. Ghosh, R. Bera, R. S. Dey, A. K. Das and C. R. Raj, *Recent Pat. Nanotechnol.*, 2010, **4**, 41–52.
50 M. Oyama, *Anal. Sci.*, 2010, **26**, 1–12.
51 S. Thiagarajan, R. F. Yang and S. M. Chen, *Bioelectrochemistry*, 2009, **75**, 163–169.
52 X. Wu, F. Zhao, N. Rahunen, J. R. Varcoe, C. Avignone-Rossa, A. E. Thumser and R. C. Slade, *Angew. Chem., Int. Ed.*, 2011, **50**, 427–430.
53 C. W. Welch and R. G. Compton, *Anal. Bioanal. Chem.*, 2006, **384**, 601–619.
54 D. A. Lowy, L. M. Tender, J. G. Zeikus, D. H. Park and D. R. Lovley, *Biosens. Bioelectron.*, 2006, **21**, 2058–2063.
55 M. Ganesana, G. Istarnboulie, J. L. Marty, T. Noguer and S. Andreescu, *Biosens. Bioelectron.*, 2011, **30**, 43–48.
56 R. Ojani, J. B. Raoof and S. Zamani, *Talanta*, 2010, **81**, 1522–1528.
57 L. Peng, S. J. You and J. Y. Wang, *Biosens. Bioelectron.*, 2010, **25**, 1248–1251.
58 X. Xie, L. B. Hu, M. Pasta, G. F. Wells, D. S. Kong, C. S. Criddle and Y. Cui, *Nano Lett.*, 2011, **11**, 291–296.
59 J. E. Mink, J. P. Rojas, B. E. Logan and M. M. Hussain, *Nano Lett.*, 2012, **12**, 791–795.
60 H. Y. Tsai, C. C. Wu, C. Y. Lee and E. P. Shih, *J. Power Sources*, 2009, **194**, 199–205.
61 J. Wang, *Electroanalysis*, 2005, **17**, 7–14.
62 T. J. Beveridge, *J. Bacteriol.*, 1999, **181**, 4725–4733.
63 M. Sára and U. B. Sleytr, *J. Bacteriol.*, 2000, **182**, 859–868.
64 B. Avasarala, R. Moore and P. Haldar, *Electrochim. Acta*, 2010, **55**, 4765–4771.
65 H. Dai, Y. W. Chi, X. P. Wu, Y. M. Wang, M. D. Wei and G. N. Chen, *Biosens. Bioelectron.*, 2010, **25**, 1414–1419.
66 X. H. Kang, J. Wang, H. Wu, I. A. Aksay, J. Liu and Y. H. Lin, *Biosens. Bioelectron.*, 2009, **25**, 901–905.
67 S. Yadav, R. Devi, P. Bhar, S. Singhla and C. S. Pundir, *Enzyme Microb. Technol.*, 2012, **50**, 247–254.
68 G. Kay and E. M. Crook, *Nature*, 1967, **216**, 514–515.
69 T. Y. Cheang, B. Tang, A. W. Xu, G. Q. Chang, Z. J. Hu, W. L. He, Z. H. Xing, J. B. Xu, M. Wang and S. M. Wang, *Int. J. Nanomed.*, 2012, **7**, 1061–1067.
70 J. Xie, M. R. MacEwan, A. G. Schwartz and Y. Xia, *Nanoscale*, 2010, **2**, 35–44.
71 A. Greiner and J. H. Wendorff, *Angew. Chem., Int. Ed.*, 2007, **46**, 5670–5703.
72 M. Seredych, D. Hulicova-Jurcakova, G. Q. Lu and T. J. Bandosz, *Carbon*, 2008, **46**, 1475–1488.
73 M. E. G. Lyons and G. P. Keeley, *Int. J. Electrochem. Sci.*, 2008, **3**, 819–853.
74 W. Jia, C. Jin, W. Xia, M. Muhler, W. Schuhmann and L. Stoica, *Chemistry*, 2012, **18**, 2783–2786.
75 J. Zhao, W. Zhang, P. Sherrell, J. M. Razal, X. F. Huang, A. I. Minett and J. Chen, *ACS Appl. Mater. Interfaces*, 2011, **4**, 44–48.
76 B. S. Shim, W. Chen, C. Doty, C. Xu and N. A. Kotov, *Nano Lett.*, 2008, **8**, 4151–4157.
77 L. Hu, W. Chen, X. Xie, N. Liu, Y. Yang, H. Wu, Y. Yao, M. Pasta, H. N. Alshareef and Y. Cui, *ACS Nano*, 2011, **5**, 8904–8913.
78 B. Moller, R. Ossmer, B. H. Howard, G. Gottschalk and H. Hippe, *Arch. Microbiol.*, 1984, **139**, 388–396.
79 Y. Zhu, L. Feng, F. Xia, J. Zhai, M. X. Wan and L. Jiang, *Macromol. Rapid Commun.*, 2007, **28**, 1135–1141.
80 T. Zhang, S. M. Gannon, K. P. Nevin, A. E. Franks and D. R. Lovley, *Environ. Microbiol.*, 2010, **12**, 1011–1020.
81 M. H. Zhou, M. L. Chi, J. M. Luo, H. H. He and T. Jin, *J. Power Sources*, 2011, **196**, 4427–4435.
82 X. Xie, G. H. Yu, N. Liu, Z. N. Bao, C. S. Criddle and Y. Cui, *Energy Environ. Sci.*, 2012, **5**, 6862–6866.
83 C. Dumas, R. Basseguy and A. Bergel, *Electrochim. Acta*, 2008, **53**, 2494–2500.
84 S. M. Strycharz, R. H. Glaven, M. V. Coppi, S. M. Gannon, L. A. Perpetua, A. Liu, K. P. Nevin and D. R. Lovley, *Bioelectrochemistry*, 2011, **80**, 142–150.

