



Enhanced microbial electrosynthesis with three-dimensional graphene functionalized cathodes fabricated *via* solvothermal synthesis



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ABSTRACT

The biological reduction of CO₂ into multicarbon chemicals can be driven by electrons derived from the cathode of a bioelectrochemical reactor via microbial electrosynthesis (MES). To increase MES productivity, conditions for optimal electron transfer between the cathode and the microbial catalyst must be implemented. Here, we report the development of a 3D-graphene functionalized carbon felt composite cathode enabling faster electron transfer to the microbial catalyst *Sporomusa ovata* in a MES reactor. Modification with 3D-graphene network increased the electrosynthesis rate of acetate from CO₂ by 6.8 fold. It also significantly improved biofilm density and current consumption. A 2-fold increase in specific surface area of the 3D-graphene/carbon felt composite cathode explained in part the formation of more substantial biofilms compared to untreated control. Furthermore, in cyclic voltammetry analysis, 3D-graphene/carbon felt composite cathode exhibited higher current response. The results indicate that the development of a 3D-network cathode is an effective approach to improve microbe-electrode interactions leading to productive MES systems.

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1. Introduction

Microbial electrosynthesis (MES) is an attractive strategy for the conversion of the greenhouse gas CO₂ into multicarbon products or methane with electrons derived from the cathode of a bioelectrochemical system (BES) [1–3]. MES reactors can be powered by an external source of electricity generated from renewable energy. Under these circumstances, one of the purposes of MES is to store electricity surpluses associated with intermittent energy sources such as wind and solar into useful products [4,5]. Interestingly, when a MES reactor is powered by solar cells or when the MES electrodes are modified to enable the direct capture of light energy, it effectively becomes an artificial photosynthesis apparatus with potentially higher solar-to-product efficiency than natural photosynthesis [1,6–9]. MES can also be driven by the

biological oxidation of pollutants at the anode effectively coupling the production of useful chemicals at the cathode with environment cleaning processes. Experimental demonstrations include sulfide removal and wastewater polishing in a bioanodic chamber generating electrons used by a microbial catalyst at the cathode to reduce CO₂ to methane or acetate [10–12].

One of the key steps of the MES process is the transfer of electrons from cathode to microbe. Successful strategies focusing on the cathode have been developed to improve electron transfer rates and production rates [4]. These include modifications of the spatial arrangement as well as of the surface of carbonaceous cathodes [13–17]. For instance, carbon cloth cathode coated with chitosan became positively charged and thus more suitable for interactions with negatively-charged microbes as demonstrated by higher cell density, electron transfer rates and acetate production rates [16]. Other cathode modifications including treatments with metallic nanoparticles, nickel nanowires or carbon nanotubes resulted in better MES performance because of better catalytic properties, enhanced surface-area-to-volume ratio and increased porosity [14–17].

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Graphene is a two-dimensional and one-atom-thick carbon material. This material has many extraordinary properties, including high electronic conductivity, low charge-transfer resistance, large specific surface area, exceptional mechanical strength and biocompatibility [18–20], which could be used to augment electron transfer rate in MES system. This has been demonstrated recently with improved MES performance observed with a carbon cloth-based biocathode modified by the injection of graphene functionalized with positively-charged tetraethylenepentamine (TEPA) [21].

Three-dimensional graphene (3D-G) formed by the coating of graphene nanosheets on a scaffold has even higher specific surface and catalytic activity [22–27]. To investigate the impact of 3D-G on MES, carbon felt (CF) cathode coated with 3D-G was fabricated *via* a solvothermal synthesis process and used to transfer electrons to a pure culture of the highly-efficient MES microbial catalyst *Sporomusa ovata* [28] for the reduction of CO₂ into acetate.

2. Experimental

2.1. Organism source and growth conditions

Sporomusa ovata DSM 2662 [29] was acquired from the Deutsche Sammlung Mikroorganismen und Zellkulturen (DSMZ). *S. ovata* strains were routinely maintained in 311 medium with 40 mM betaine as substrate under a N₂-CO₂ (80:20) atmosphere. For growth with H₂ as the electron source and CO₂ as the carbon source, no betaine was added to the 311 medium and the atmosphere was N₂-CO₂-H₂ (83:10:7). For all growth conditions presented in this study, casitone, sodium sulfide, yeast extract, and resazurin were omitted from the 311 medium. For bioelectrochemical experiments, cysteine was also omitted from the 311 medium.

2.2. Synthesis of graphene oxide (GO)

GO was prepared by a two-step synthetic procedure as reported previously [30,31]. Pre-oxidized graphite was prepared in the first step and in the next step GO was obtained through exfoliation and strong oxidation. In the first step, graphite powder (10 g) was added to a concentrated H₂SO₄ solution (7.5 ml) containing K₂S₂O₈ (2.5 g) and P₂O₅ (2.5 g) and kept in a hot water bath (80 °C) under strong stirring for 3 hours. After being cooled down to room temperature, the dark green mixture was diluted with Milli-Q water. The mixture was then filtered before being washed several times with Milli-Q water until the washed out solution had a neutral pH. The pre-oxidized graphite powder was then collected and air-dried overnight at room temperature.

In the second step, pre-oxidized graphite powder (1.0 g) was added to H₂SO₄ solution (25 ml) and maintained at 0 °C. KMnO₄ (3.0 g) was added to the mixture under slow stirring while the temperature was below 20 °C. The mixture was then heated at 35 °C under continuous stirring for 2 hours before the addition of Milli-Q water (46 ml). After two minutes, a 0.5% H₂O₂ (140 ml) solution was added to the mixture and the solution color changed immediately to bright yellow. The mixture was filtered and then the retained material was washed thoroughly with 10% HCl solution (250 ml) to remove residual metal ions. The filtered-out material was resuspended into Milli-Q water before being centrifuged at 12000 rpm in a benchtop centrifuge. The supernatant containing highly dispersed and stable GO nanosheets was collected. To remove residual salts and acids, the sample was dialyzed using a dialysis tube (cut-off molecular weight of 12–14 kDa) for one week by regularly replacing the water in a water bath with fresh Milli-Q water 4 times per day.

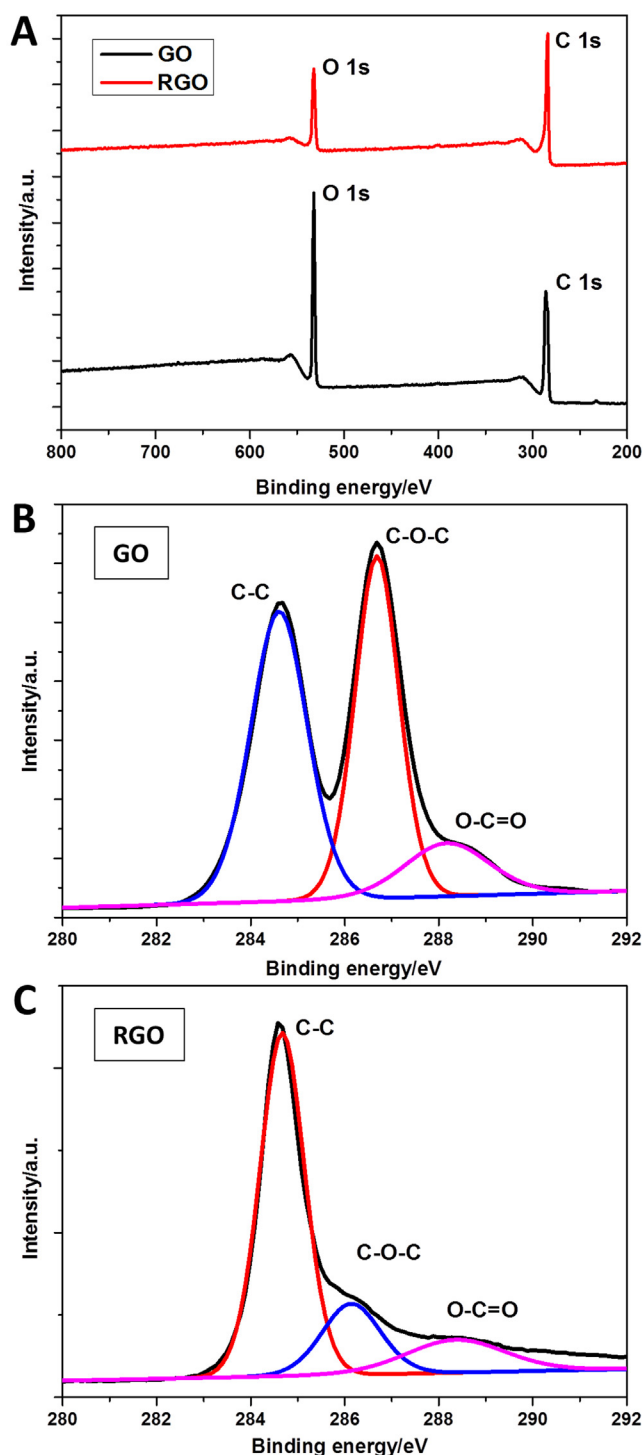


Fig. 1. Comparison of XPS spectra of GO and RGO with the survey spectra (A) and the C 1s XPS spectra (B–C).

2.3. Reduction of GO and fabrication of 3D-graphene (3D-G) cathode electrodes

CF electrodes (Jiangsu Tongkang Special Activated Carbon Fiber & Fabric Co., Ltd, China) were pretreated with 3 M HNO₃ for 12 hours and then extensively washed with Milli-Q water [16]. The acid treated electrodes were dried by nitrogen gas flow, prior to modification with 3D-G.

The biocompatible reduction of GO and the fabrication of 3D-G coated CF cathode was done in a single step *via* a solvothermal

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