Abstract

The major objective of the present study is to develop an efficient photosynthetic microbial fuel cell (PMFC) using cyanobacteria as anodic catalyst with a further aim of utilizing this energy generating device for sensing applications. One of the key issues to make the bacterial catalysts effective for generating power in microbial fuel cell is the proper electrical communications between the bacterial cells and the conductive electrode of the fuel cell device. We proposed the direct electron transfer (DET) as the guiding principle for channelizing the cellular electrons to the anode for which, setting up of cyanobacteria biofilm on the anode was considered as a suitable strategy to comply the principle. We explored different synthetic and natural polymeric thin films for their rapid biofilm promoting abilities of cyanobacteria, *Synechococcus* sp. For a comparative analysis, the study was extended to two commonly available bacteria, namely, *Escherichia coli* and *Lactobacillus plantarum*. The activating role of different polymer thin films coated over polystyrene support on the *Synechococcus* sp. biofilm growth was examined concurrently by measuring biofilm florescence using a dye and by measuring cell density in the isolated biofilm. Compared to blank (no coating), the increase in biofilm formation (%) on silk, chitosan, silk-chitosan (3:2) blend, polyaniline, osmium, and Nafion films were 27.73 (31.16), 21.55 (23.74), 37.21 (38.34), 5.35 (8.96), 6.70 (6.55) and (nil), respectively with corresponding cell density (%) shown in the parentheses. This trend of biofilm formation on the films did not significantly vary for *E. coli* and *L. plantarum* strains. The films of 20 residues long each of glycine-alanine repeat peptide, which mimics a silk fibroin motif, and a hydrophobic glycine-valine repeat peptide, increased the biofilm growth by 13.53 % and 26.08 %, respectively. Silk and blend films exhibited highest adhesion unit (0.48 to 0.49), adhesion rate ((4.2 to 4.8) $\times 10^{-6}$, m s^{-1}) and Gibbs energy of adhesion (-8.5 to -8.6 kT) with *Synechococcus* sp. The results confirmed interplay of electrostatic and hydrophobic interaction between cell-surface and polymer films for promoting rapid biofilm growth. This study established that the thin films of silk and the blend (3:2) promoted rapid biofilm growth for all the tested micro-organisms. This positive trait of silk-film was then implemented to develop biofilm on the anodic surface of the PMFC where the silk fibroin (SF) was rationally doped with CdTe quantum dots (QD) and graphene nanoplatelets (GNP) to enhance and stabilize the photocurrent in the PMFC. The nanocomposite matrix supported biofilm growth of the photo-catalyst *Synechococcus* sp., surged the bacterial photo systems (PS

I and PS II) with appropriate light ($\lambda_{650 - 750\ nm}$) at a broad excitation spectrum ($\lambda_{350 - 644\ nm}$) through fluorescence resonance energy transfer (FRET) and facilitated the metabolic electron relay through DET to the anode during operation of the PMFC. The maximum current density of the PMFC obtained with the nanocomposite bioanode (1.89 A m^{-2}) was ~ 5.7 fold higher than the corresponding blank graphite anode. The positive effect of QD was further confirmed from the fading reversal of polarity during the circadian cycle leading to sustained current generation in the PMFC. The SF with the highest band gap of 4.09 eV and GNP with the lowest band gap of -3 eV, were finally compromised to a band gap energy of 2.9 eV in the nanocomposite matrix. The GNP decreased the charge transfer resistance by ~ 9 fold that facilitated DET as evident from the appearance of a pair of redox peak of the bioanode in the voltammogram with a formal potential of -156 mV. Structural studies demonstrated rational interactions of the hydrophobic β-sheet of the SF with the nanomaterials. An unprecedented light conversion efficiency of 4.01 % for the cyanobacteria was achieved with the nanocomposite bioanode based PMFC. The developed PMFC was then evaluated for its biosensing application using alcohol as target analyte. A novel signal in the form of potential burst against the substrate alcohol was identified. The origin of the potential burst was attributed to the bacterial membrane depolarization caused by the interaction with the substrate. The magnitude of the PMFC burst potentials was well correlated to the alcohol concentration with a dynamic range of 0.001 to 20 % and LOD of 0.13 % (R^2 = 0.96). The device exhibited higher selectivity towards ethanol than methanol as discerned from the corresponding cell-alcohol interaction constant (K_i) of 780 mM and 1250 mM. The concept when translated to a paper-based PMFC (p-PMFC) (size ~ 20 cm^2), the device exhibited shelf-life of ~ 3 months, detected ethanol within 10 s with a dynamic range of 0.005 to 10 % and LOD of 0.02 % (R^2 = 0.99). This novel approach with portable format has great application potential for selective, sensitive and rapid detection of alcohol.