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Environmentally Benign Energy Harvesting Biophotovoltaic Cells with Carbon Shell-Encased Fe_3O_4 Nanoparticles in CNTs

Chandrasekaran Karthikeyan, Fong-Lee Ng, Selvavinayagam Sutharsun, Asad Syed, Ali H. Bahkali, Melvin Victor De Poures, Vengadesh Periasamy, Yang Xia, Georgepeter Gnana kumar,* and Siew-Moi Phang*

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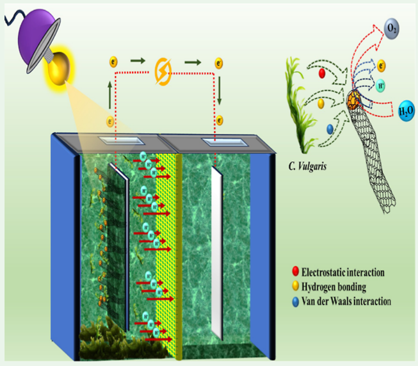
ABSTRACT: Carbon nanotubes (CNTs) comprising carbon-shell-confined iron oxide (Fe_3O_4) nanoparticles (Fe_3O_4/CNT) are synthesized through the chemical vapor deposition method, employing a catalytic tip-growth mechanism. The rationale behind the formation of Fe_3O_4/CNT nanostructures from the catalytic growth of Fe_3O_4 nanoparticles is investigated using diverse morphological and structural characterization techniques, and the impacts of these nanostructures' properties on green energy generation in the biophotovoltaic (BPV) system are assessed using a range of electroanalytical methods. The substantial oxidation current witnessed from the cyclic voltammograms of processed electrodes discloses the existence of electroactive proteins in microalgae. The dominance of water photolysis reaction on BPV energy generation compared to the metabolism of organic substrates is substantiated from the scrutinized voltammograms. The extracellular polymeric substances secreted by *Chlorella vulgaris* cells effectively bind with Fe_3O_4 nanoparticles via hydrogen bonding, electrostatic, and van der Waals interactions, which presumably improves the kinetics of the involved electrochemical reactions. Furthermore, the integration of carbon shell-encased Fe_3O_4 nanoparticles in CNTs capitalizes on the strengths of each component-offering protection and stability through the aligned porous carbon walls, enhanced electrical conductivity via both the CNTs and proximity between the Fe_3O_4 core and carbon shell, and increased catalytic activity from the Fe_3O_4 nanoparticles, augmenting the maximum BPV power generation. The high BPV operational stability scrutinized for Fe_3O_4/CNT is corroborated to the protective graphitic layer-encased Fe_3O_4 nanoparticles, limiting the aggregation and disintegration of electroactive sites and structural deformation of tubular nanostructures in stringent BPV conditions. The excellent BPV performance exhibited by the Fe_3O_4/CNT establishes it as one of the most efficient anode materials reported to date, reflecting its substantial potential in steering the advancement of next-generation sustainable energy conversion technologies.



KEYWORDS: *charge recombination, delocalized electrons, extracellular polymeric substances, hydrogen bonding, sp^2-bonded network*

1. INTRODUCTION

The limited subsistence of fossil fuel reserves and their concomitant combustion contribute, respectively, the global energy crisis and greenhouse effect, provoking pressing demands toward the development of sustainable energy conversion devices.[1,2] Harnessing bioenergy from photosynthetic components via biophotovoltaic (BPV) cells is deemed an appealing strategy to cope with the energy demand while considering ecological concerns.[3] The constructive characteristics of BPVs including self-repair, no fuel replenishment, energy conversion capability under day/night operations, absence of toxic byproducts, etc., endorse their relevance as a sustainable energy conversion device.[4]

Accordingly, a wide spectrum of biological materials such as cyanobacteria,[5] purple bacteria,[6] thylakoid membranes,[7] and green algae[8,9] has been extensively explored as photosynthetic components in BPV systems. Among these, green algae—most notably *Chlorella vulgaris*—are regarded as a leading biocomponent in BPV systems, attributed to their exceptional photosynthetic efficiency and accelerated proliferation rate.[8] These advantages stem from the presence of both Photosystem I (PSI) and Photosystem II (PSII), a dual-photosystem configuration that facilitates superior light harvesting and efficient electron transfer.[8,9] It significantly augments the photoconversion efficiency, facilitating the seamless transformation of solar energy into electrical output while maintaining a sustained and reliable biomass supply. In contrast, purple bacteria, which depend on the comparatively

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