

Single-walled carbon nanotube forest with hydrogenase for electrochemical hydrogen evolution

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In this study, a high-efficiency hydrogen evolution system was successfully developed using hydrogenase (H₂ase) and a single-walled carbon nanotube forest (SWNT-F) without any chemical mediators. Hydrogenase (H₂ase) is the key enzyme in hydrogen metabolism in many microorganisms and catalyzes the reversible reaction of hydrogen and proton. An oxygen-tolerant H₂ase from the phototropic bacterium *Thiocapsa roseopersicina* needs some appropriate electron carrier to catalyze proton to H₂, such as cytochrome *c*₃ and methyl viologen (1). And H₂ase can be utilized as a catalyst in the controlled potential electrolysis sensor to detect molecular hydrogen dissolved in a solution (2).

Single-walled carbon nanotubes of excellent conductivity and mechanical strength are expected as materials being combined with the biological molecule. SWNT-F was successfully grown with water-assisted chemical vapor deposition resulting in massive growth of superdense and vertically aligned nanotube forests with heights up to 2.5 millimeters (3).

In this study, H₂ase was immobilized on SWNT-F which has the patterned and highly organized intrinsic structure (Fig. 1). Hydrogen production using H₂ase-SWNT-F electrode was investigated. In this system, SWNT-F was used as the electron transfer mediator and adsorbent making the H₂ase density high in reacting unit for a high-efficiency H₂ evolution. The immobilization of the H₂ase protein into the SWNT-F is very simple. The protein can be naturally introduced into the inside of SWNT-F by capillarity.

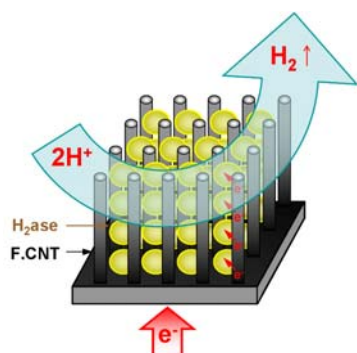


Fig. 1 A schematic diagram of the system for H₂ evolution using H₂ase with SWNT-F

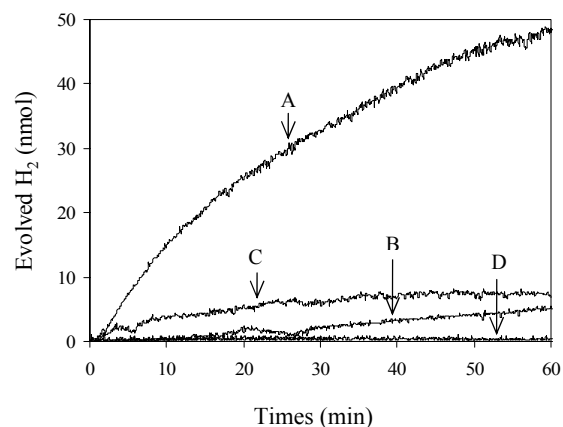


Fig. 2 Electrochemical hydrogen evolution using H₂ase-SWNT-F glassy carbon electrode (A) in comparison with the control electrode of H₂ase with commercial SWNT (B), H₂ase without SWNT-F (C) and no H₂ase with SWNT-F (D).

To analyze the activity of H₂ evolution, a four-electrode system was used. It consisted of commonly used three-electrodes (w; glassy carbon (GC), r; Ag/AgCl, c; platinum) with a hydrogen electrode to measure hydrogen concentration in a cell-chamber (Biott, Tokyo, Japan). The measurement was performed in 50 mM phosphate buffer (pH6.8) at room temperature. The H₂ase-SWNT-F was immobilized simply on GC by using a cellulose membrane.

The potential of GC electrode was kept at -700 mV (vs Ag/AgCl). As shown in Fig. 2, hydrogen concentration immediately increased by using the H₂ase-SWNT-F electrode. The efficiency of H₂ evolution by using the H₂ase-SWNT-F electrode without any mediators resulting V_{\max} of 6.1 nmol/min about 80 times higher than that of the previous device using chemical mediators (2). SWNT-F efficiently functioned as a protein holder and an electron mediator from GC to H₂ase. This result suggests that SWNT-F have a potential to be applied for the various redox proteins.

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