Adaptive nanowire–nanotube bioelectronic system for on-demand bioelectrocatalytic transformations†

Rawiwan Laocharoensuk,[a] Andrea Bulbarello,[ab] Saverio Mannino[b] and Joseph Wang*[a]

Received (in Cambridge, UK) 1st June 2007, Accepted 4th July 2007
First published as an Advance Article on the web 23rd July 2007
DOI: 10.1039/b708313k

An integrated nanobioelectronic system, exploiting the distinct properties of nanowires and carbon-nanotubes, has been designed for triggering reversibly and on-demand bioelectrocatalytic transformations of alcohols.

The emergence of nanotechnology has opened new horizons for the application of nanomaterials. Even though there has been tremendous progress in the development of various nanomaterials, little attention has been given to functional nanosystems, integrating several nanomaterials. Such integrated systems should lead to new and unique operations, taking advantage of the distinct properties of their individual nanomaterial components.

Here we report on an adaptive nanomaterial bioelectronic system, integrating nanowires (NW) and carbon-nanotubes (CNT), for on-demand bioelectrocatalytic transformations. Magnetic control of bioelectrocatalytic processes was pioneered by Willner's group that used the attraction and retraction of functionalized magnetic spheres for ON–OFF switching of enzymatic reactions.[1] Recently we demonstrated the ability of Ni–Au nanowires, functionalized with glucose oxidase, for modulating on-demand the bioelectrocatalytic oxidation of glucose in connection to a surface-bound ferrocene mediator.[2] The integrated NW–CNT system, described in the present communication, relies on alcohol-dehydrogenase (ADH) functionalized Ni–Au–Ni nanowires and a CNT-modified amperometric transducer (Fig. 1; see Electronic Supplementary Information† for experimental details). Switching the orientation of the nanowires from vertical to horizontal (in the presence of the substrate and NAD^+ cofactor) brings the enzyme (and its NADH product) to the CNT coating, which promotes the electrocatalytic detection of NADH[3] (see inset for the corresponding cyclic voltammogram) and the regeneration of NAD^+ essential for enabling the continuous bioelectrocatalytic turnover. As will be demonstrated below, both the NW and CNT are required for such an on-demand bioelectrocatalytic process. The new concept of an adaptive NW–CNT system is illustrated below for switchable bioelectrocatalytic transformations of ethanol, as well as for parallel biosensing of ethanol and methanol in connection to the co-immobilization of ADH and alcohol oxidase (AOX). Besides sensing applications, the new NW–CNT based adaptive operation offers great promise for regulating the operation of biofuel cells or bioreactors.

The ability to trigger and modulate reversibly the enzymatic reaction of ethanol is illustrated in Fig. 2C which displays current–time recording at +0.45 V obtained during cyclic vertical-to-horizontal reorientations of the Ni/ADH–Au/Ni nanowires. Reversible changes in the NADH oxidation current are observed upon switching the surface orientation of the nanowires between the vertical (c) and horizontal (b) positions, reflecting the triggered bioelectrocatalytic transformation of ethanol in the horizontal alignment. In contrast, no bioelectrocatalytic oxidation is observed in control experiments without the CNT coating (A) or the ADH functionalization (B). Also shown (D) is the corresponding magnetoswitchable response obtained by holding the bare glassy-carbon surface at +0.90 V. While this potential allows oxidation of the enzymatically-generated NADH at the uncoated surface, it results in progressively smaller current changes during repetitive reorientations, reflecting the gradual surface fouling and deactivation (owing to adsorption of dimeric and other oxidation products).[4] In contrast, the reproducible magnetoswitchable current changes observed at the CNT-coated surface (C) reflect its high resistance to passivation and the electrochemical regeneration of NAD^+.[3,5] Apparently, both the bi-functionality of the Ni–Au nanowires [providing the magnetic alignment (Ni) and enzyme carrier (Au)] and the stable electrocatalytic function of

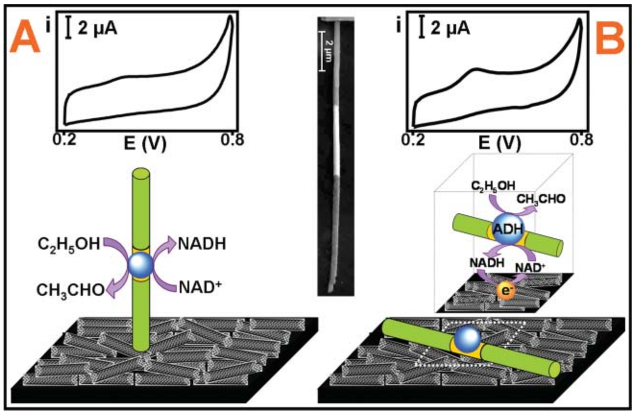

Fig. 1 On-demand magnetically-triggered bioelectrocatalytic transformations of ethanol. The NW–CNT based activation of ADH involves Ni/ADH–Au/Ni nanowires in connection to a CNT-coated surface and changes in the nanowire orientation between the vertical (A) and horizontal (B) positions for blocking and activating the bioelectrocatalytic process, respectively. Insets show the corresponding cyclic voltammograms. Also shown (center) is an SEM image of the three-segment nanowire.

---

[a] *Departments of Chemical Engineering, and Chemistry and Biochemistry, The Biodesign Institute, Arizona State University, Tempe, AZ 85287-5801, USA. E-mail: joseph.wang@asu.edu; Tel: 1-480-727-0399*
[b] *Department of Food Science and Technology, Universitá degli Studi di Milano, 20133 Milano, Italy*

† Electronic supplementary information (ESI) available: Experimental details. See DOI: 10.1039/b708313k

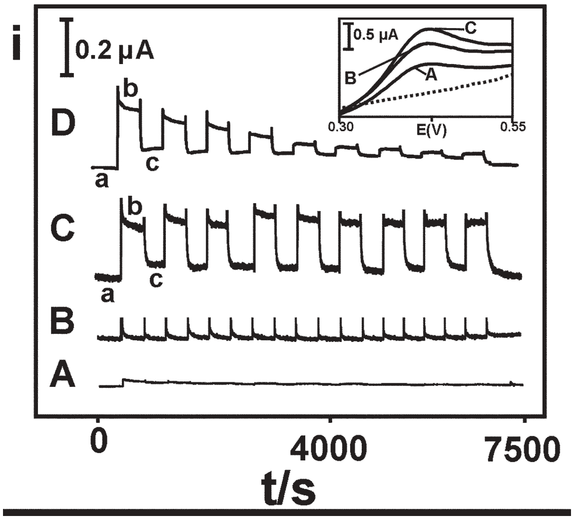

Fig. 2 Reversible on-demand magnetoswitchable bioelectrocatalytic transformations of ethanol through cyclic vertical-to-horizontal reorientations of the Ni/ADH–Au/Ni nanowires. Amperometric signals for 10 mM ethanol using (A, D) the Ni/ADH–Au/Ni nanowires but without the CNT coating; (B) the CNT surface modification but without anchoring the ADH; (C) with both ADH on the NW and the CNT on the surface. Magnetic modulation with the nanowires in the "off" (a), horizontal (b) and vertical (c) positions. Working potential: +0.45 V (A–C) and +0.90 V (D) *vs.* Ag/AgCl; electrolyte, 0.1 M phosphate buffer (pH 7.4). Inset shows cyclic voltammograms for the magnetically-triggered bioelectrocatalytic reaction using increasing ethanol concentrations (5–15 mM; A–C), along with the background voltammogram (dotted line), with Ni/ADH–Au/Ni nanowires oriented in the horizontal position. Scan rate, 10 mV s^{-1}.

the CNT are essential for activating reversibly the enzymatic reaction of ethanol. Acid-purified CNT, such as those used in the present study, contain oxygenated groups (*e.g.*, quinone) on their surface[6] that can promote the electrocatalytic oxidation of NADH, recycling of the NAD$^+$ cofactor, and the turnover of ethanol.[5,7] As indicated from the inset of Fig. 2, increasing the ethanol concentration (in 5 mM steps) results in well-defined cyclic voltammograms, with the NADH oxidation current (at E_p = +0.42 V) increasing in magnitude as the ethanol concentration is elevated (A–C). The use of three-segment nanowires, with the enzyme anchored to the central gold segment, ensures that the ADH does not contact the CNT surface in the vertical orientation.

It is possible also to functionalize the adaptive nanowires with two enzymes for the parallel sensing of two alcohols. As illustrated in Fig. 3, such dual analysis of two substrates relies on the co-immobilization of ADH and AOX onto the gold segment for activating on demand the bioelectrocatalytic transformations of ethanol and methanol, respectively. Oxidation of ethanol and methanol in the presence of the corresponding enzyme (ADH and AOX) and co-substrate (NAD$^+$ and O_2, respectively) results in the generation of NADH and hydrogen peroxide, respectively. Selective analysis of the two alcohols can be accomplished by monitoring the CNT-promoted electrocatalytic signals of their NADH and hydrogen peroxide products during the horizontal alignment of the nanowires (Fig. 4B).

Such on-demand dual ethanol and methanol analysis is illustrated in Fig. 4. As expected,[3,8] the CNT-modified surface promotes the oxidation of both NADH (Fig. 4A(a)) and hydrogen peroxide (Fig. 4A(b)), with the two redox signals observed at different potentials (around 0.42 and 0.70 V, Fig. 4A(c)). Similar redox signals are observed in Fig. 4B with the ADH/AOX-bifunctional nanowires in the horizontal position, in the presence of ethanol (a), methanol (b) and of both alcohols (c). In contrast, substantially smaller signals are observed upon reorienting the bienzyme-nanowires into the vertical position (C).

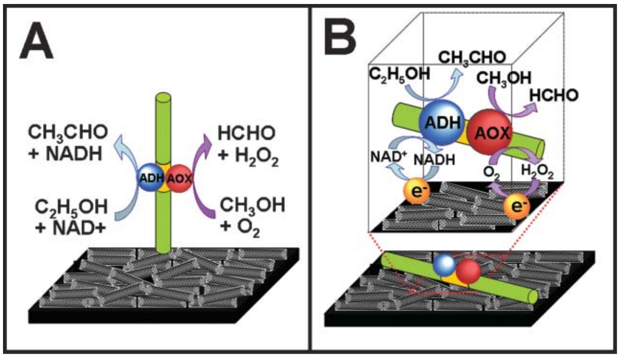

Fig. 3 Parallel on-demand biosensing of ethanol and methanol using Ni–Au–Ni nanowires functionalized with the ADH and AOX, and CNT-promoted electrocatalyic detection of NADH or hydrogen peroxide products. Bi-enzyme (ADH–AOX) functionalized nanowires in the vertical (A) and horizontal (B) positions, along with the CNT-coated transducer.

In conclusion, we have demonstrated that the coupling of nanowires and CNT can lead to on-demand bioelectrocatalytic transformations of alcohols. Such an adaptive magnetoswitchable nanobioelectronic system exploits the distinct properties of its individual nanomaterial components, can be extended to a wide range of biocatalytic systems, and offers great promise for regulating the operation of biofuel cells, bioreactors, and biosensing devices in response to specific needs.

This work was supported by the National Science Foundation (Grant Number CHE 0506529). AB and RL acknowledge fellowships from the University of Milan (Italy) and DPST project (Thailand), respectively.

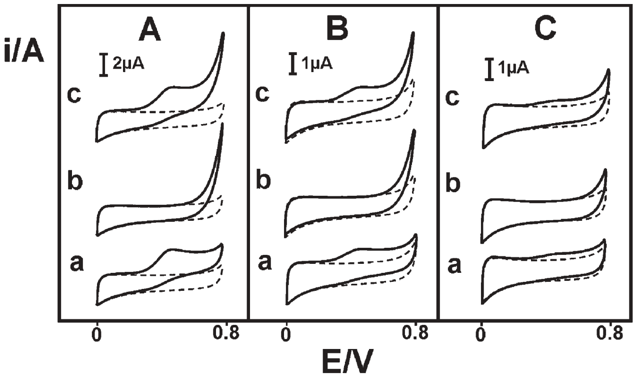

Fig. 4 Magnetically-triggered bioelectrocatalytic transformations of ethanol and methanol using the Ni/ADH–AOX–Au/Ni nanowires. Cyclic voltammograms (A) for 1 mM NADH (a), H_2O_2 (b) and a mixture of both (c) at the CNT-coated transducer without Ni/Au/Ni nanowires; (B) for 10 mM ethanol (a), methanol (b) and both at the CNT-coated transducer with bi-enzyme nanowires in the horizontal position; (C) same as B, but with nanowires in the vertical position. Other conditions, as in Fig. 2 (inset).

Notes and references

1 I. Willner and E. Katz, *Angew. Chem., Int. Ed.*, 2003, **42**, 4576.

2 Ó. A. Loaiza, R. Laocharoensuk, J. Burdick, M. Rodriguez, J. Pingarron, M. Pedrero and J. Wang, *Angew. Chem., Int. Ed.*, 2007, **46**, 1508.

3 M. Musameh, J. Wang, A. Merkoci and Y. Lin, *Electrochem. Commun.*, 2002, **4**, 743.

4 J. Wang, L. Angnes and T. Martinez, *Bioelectrochem. Bioenerg.*, 1992, **29**, 215.

5 S. Liu and C. Cai, *J. Electroanal. Chem.*, 2007, **602**, 103.

6 A. Kuznetsova, I. Popova, J. T. Yates, M. J. Bronikowski, C. B. Huffman, J. Liu, R. E. Smalley, H. H. Hwu and J. G. Chen, *J. Am. Chem. Soc.*, 2001, **123**, 10699.

7 H. Jaegfeldt, T. Kuwana and J. Johansson, *J. Am. Chem. Soc.*, 1983, **105**, 1805.

8 J. Wang, M. Musameh and Y. Lin, *J. Am. Chem. Soc.*, 2003, **125**, 2408.