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Magnetic Tuning of the Electrochemical Reactivity through Controlled Surface Orientation of Catalytic Nanowires

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Recently, we have witnessed considerable interest in the magnetic control of the electrical properties of electrode interfaces, including reversible activation and blocking of electrochemical and bioelectrochemical processes.[1−4] Such "on/off" switching of electrode reactions has been accomplished by magnetic attraction and retraction of microscopic magnetic particles to and from electrode surfaces. While most of this early work focused on functionalized magnetic spheres, we demonstrated recently that the magnetic and electrocatalytic properties of nickel microparticles can be exploited for magnetoswitchable control of the electrochemical reactivity without the need of functionalized ferromagnetic particles.[4]

Here we wish to report for the first time on the application of nanowires for magnetic control of the electrochemical reactivity and to demonstrate how one can modulate the electrocatalytic activity by orienting catalytic nanowires at different angles. Nanowires have received considerable attention owing to their broad potential applications[5] but not for magnetic control of electrochemical processes. Unlike early on/off magnetic switching studies,[1−4] the present magnetoswitchable protocol relies on modulating the electrochemical reactivity without removing the magnetic material from the surface (Figure 1). Such capability may be extremely useful for adjusting the electrochemical reactivity, such as for tuning the power output of fuel cells (rather than switching the power on/off[6]). Magnetic directionality of nanowires was used recently toward their assembly into complex structures[7] and the creation of catalytic nanomotors,[8] but not for modulating electrochemical processes.

The ability to use nanowires for magnetic control of electrochemical processes is illustrated in Figure 2 in connection to electrocatalytic measurements of glucose and methanol using catalytic nickel nanowires. Nickel is known for its magnetic properties and electrocatalytic action toward aliphatic alcohols, carbohydrates, and amino acids.[4,9] The 200 nm diameter, 6 μm long nickel nanowires were prepared by the membrane template-directed electrodeposition.[10] Shown in Figure 2 is the amperometric response for glucose (A) and methanol (B) in the absence of the nanowires (a) and with the nanowires magnetically oriented in the "vertical" (b) and "horizontal" (c) positions. As expected, a small background response is observed at +0.85V in the absence of the magnetic field and hence of the nanowires on the carbon substrate (a). Positioning the nanowires on the surface of the thick-film carbon electrode, with the magnetic field in the vertical orientation, leads to a dramatic enhancement of the signal (b), reflecting the catalytic action of the nanowires.[4] A substantial decrease of this response is observed upon switching the magnetic field and, in turn, the nanowires from the vertical to the horizontal position (c). The current returns to its higher value upon reorienting the nanowires to the vertical position (b). As indicated from Figure 2, such magnetically modulated redox transformations can be repeated multiple times upon repetitive changes of the surface orientation. The corresponding signal changes are highly reproducible and fast. Following six such reorientation cycles, the magnetic field was removed, retracting the nanowires from the surface, and returning the response to its background value (a).

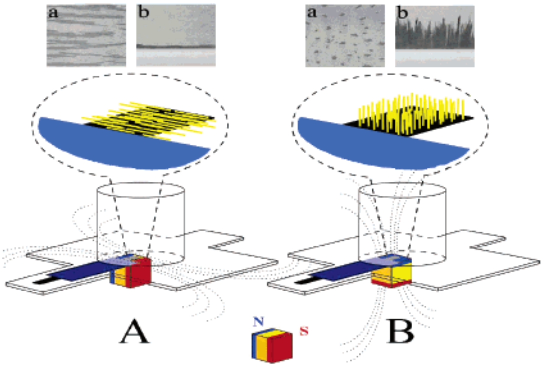

Figure 1. The experimental setup involving nickel nanowires for the magnetic control of electrocatalytic processes, with the magnetic field in the horizontal (A) and vertical (B) positions. The nanowires orient parallel to magnetic field lines. An external magnet, positioned below the electrode, was used for changing the orientation of the magnetic field. Also shown (top) are split optical images of the surface with top (a) and side (b) views of the nanowires.

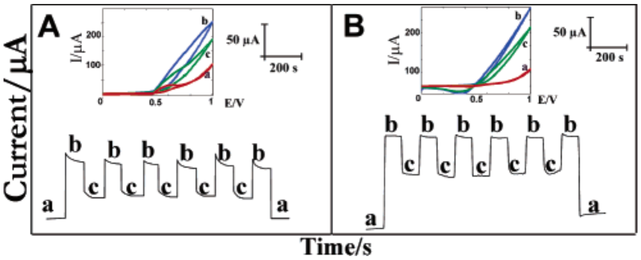

Figure 2. Amperometric response for 1 mM glucose (A) and methanol (B), in the absence of the nanowires (a), and with the nanowires oriented in the vertical (b) and horizontal (c) positions. Potential, +0.85 V (vs Ag/AgCl); electrolyte, 0.4 M NaOH. Also shown (insets) are cyclic voltammograms for 25 mM glucose (A) and methanol (B) using the corresponding magnetic fields and a scan rate of 100 mV s^{-1}.

Also shown in Figure 2 (insets) are cyclic voltammograms for glucose (A) and methanol (B) using the corresponding nanowire orientations. As expected, a small response is observed over most of the potential window in the absence of the nanowires (a). In contrast, the magnetic attraction of the catalytic nanowires to the surface leads to a defined voltammetric response, starting around 0.50 V, characteristic of nickel electrodes.[4,9] Notice again the larger response associated with the vertical orientation (b vs c). The voltammetric response was reproducibly switched between the low and high states by cyclic reorientation of the nanowires between the vertical and horizontal positions (not shown).

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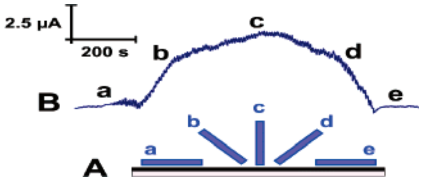

Figure 3. Tuning of the electrode activity through control of the angle of the nanowire orientation (a−e). (B) Amperometric response for 1 mM glucose recorded while changing slowly the orientation of the nanowires from the horizontal (a) through vertical (c) and back to horizontal (e). Potential and electrolyte, as in Figure 2. Magnet−surface distance, 1 cm. Also shown (A) are the corresponding nanowire−surface angles.

The reversible switching between the two surface orientations of the nanowires is indicated from digital optical images of Figure 1 (top). These images show aggregated nanowire structures in the horizontal (A) and vertical (B) positions from directly above (a) and tangent to (b) the electrode surface. Such magnetically oriented aggregated nanostructures result from the attractive forces between nanowires. The top view of the horizontal nanowires (A,a) indicates that the nanowire structures appear as “bands” spread across the electrode surface, as opposed to the “island-like” bundle structures in their vertical position (B,a).

Such magnetic modulation of electrochemical transformations reflects changes in the accessibility of the glucose and methanol solutes to the nickel catalytic sites upon switching between the two surface orientations. While the catalytic sites are fully accessible to the solute in the vertical orientation, switching to the horizontal position partially “blocks” them, hindering the solute transport to the portion of the nickel surface facing the carbon support. Such surface effects are opposite to what is expected due to magnetohydrodynamic effects which are pronounced when the magnetic field is parallel to the electrode surface (i.e., when the nanowires are in the horizontal position) and negligible when perpendicular.[11] Another indication that the behavior of Figure 2 is due predominantly to surface effects is the observation (not shown) that such magnetically modulated response is minimal with substantially shorter nanowires (for which the change in the accessible surface area is expected to be less profound). Apparently, nanowires with different aspect ratios would be useful for tuning the electrochemical reactivity. A cubic external magnet was used to ensure that the changes in the orientation of the magnetic field are not coupled to changes in the electrode−magnet distance (i.e., in the magnetic flux density B).

In addition to reversibly switching between two surface orientations, it is possible to gradually change the angle of the nanowire orientation and accordingly the current output. For this purpose, the external magnet was mounted to a stepper motor that allowed a controlled change of the orientation of the magnetic field (over 180°) and hence a gradual change of the orientation of the catalytic nanowires (Figure 3A). Such control of the nanowire surface angle allows fine-tuning of the electrocatalytic activity. For example, Figure 3B displays the amperometric response for glucose recorded continuously while changing the surface orientation of the nanowires (from horizontal through vertical and back to horizontal positions). The current changes in a nearly parabolic fashion upon increasing the angle of the surface orientation. It reaches its maximum value at the vertical position (c) and gradually returns to the reduced horizontal response (a, e). Such ability to tune the electrode activity is attributed primarily to changes in mass transport [due to tortuosity (τ) effects], from the maximum flux in the vertical position. This explanation is supported by the semicircle spectrum of Figure 3B, with the current proportional to $(\sin \theta)^2$, θ being the orientation angle. A parabolic profile is expected for tortuosity-dependent flux, where the current depends on the inverse of the square of the tortuosity (i α $1/\tau^2$), with the tortuosity equals to $1/\sin \theta$.[12] While diminished mass transport appears to be the dominating factor, surface area blocking effects may account for part of the observed behavior, particularly upon approaching the horizontal position. Similar accessible surface areas are expected for the different angles (except at 0 and 180°). This is supported by the corresponding background voltammograms and amperogram (see Figure 1 in Supporting Information). The movie shown in the Supporting Information illustrates that the nanowire bundles are preserved during the stepwise switching between the horizontal and vertical positions. The current profile of Figure 3B indicates that smaller modulations in the current output could be achieved through small steps in the nanowire orientation.

In conclusion, we have demonstrated the use of nanowires for magnetoswitchable control of electrochemical processes. In contrast to early studies involving magnetic spheres and on/off switching of electron-transfer reactions, the present protocol relies on modulating the electrochemical reactivity without removing the catalyst from the surface. Such behavior has been attributed to the reversible blocking of the redox processes and to changes in the tortuosity-dependent flux rate. We are exploring this capability for controlling the operation of fuel cells and extending it to biofunctionalized nanowires for modulating biocatalytic reactions.

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Supporting Information Available: Related instrumentation, reagents, procedures, and additional data and movies. This material is available free of charge via the Internet at http://pubs.acs.org.

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