

On-Demand Protection of Electrochemical Sensors Based on Adaptive Nanowires

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Electrochemical sensors provide unlimited opportunities for monitoring health and making the world safer and cleaner.^{1,2} Such devices meet the environmental and security demands for monitoring electroactive pollutants or threat agents with high sensitivity, selectivity, and temporal resolution.^{3,4} A major problem in practical applications of electrochemical sensors systems stems from the adsorption of surface-active materials onto the working electrode.^{5–7} The adsorption causes an electrode fouling, resulting in severe suppressions and distortions of the voltammetric peaks. Such surface fouling has proved to be the major barrier to the development of reliable continuous monitoring devices. Various protective coatings, such as Nafion⁶ or agarose gel,⁷ have been proposed for excluding surface-active macromolecules and minimizing surface-fouling effects. Surprisingly, little effort has been devoted to the development of “smart” sensors that are able to change their operation for addressing the surface fouling problem of electrochemical devices.

This Communication reports on the use of adaptive nanowires for the on-demand protection of electrochemical (stripping-voltammetric) sensors for trace metals. Adaptive sensor systems, pioneered by Diamond's group,^{8,9} offer great promise for changing the operation of sensors in response to a specific need (threat, opportunity, etc.). Such systems can reversibly modulate the surface properties under an external stimulus and can reconfigure themselves based on the results. Hydrophobic magnetic spheres were used by Katz et al.¹⁰ for reversible inhibition of DNA reactions. The nanowire-based adaptive protective system, presented in this paper, offers periodic exposure of the surface (during the measurement step) and setting the sensor in the protective (passive) mode between repetitive measurements (Figure 1). This is accomplished by switching magnetically the surface orientation of alkanethiol-coated gold nanowires, containing a short nickel (magnetic) segment, between vertical and horizontal positions. This leads to “opening” and “closing” of the surface, respectively, to allow the measurement and protect the transducer between repetitive runs.

The ability to switch on-demand the operation of electrochemical metal sensors between active and passive modes offers substantial improvements in their stability in the presence of common surfactants. Such on-demand protection capability is illustrated in Figure 2 that compares the stripping-voltammetric cadmium signals in the presence of gelatin (A) and Tween 80 (B) recorded at 5 min intervals at the bare (a) and nanowires-coated (b) electrodes. The bare electrode displays a substantial diminution of the cadmium peak in the presence of both surfactants. A rapid decrease of the response (of ca. 70% within 10 min) is observed using the gelatin solution, while a gradual one, of up to 55% within 60 min, is

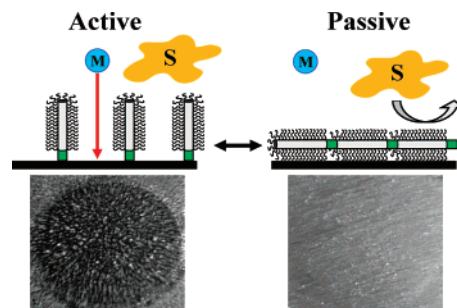


Figure 1. On-demand protection of an electrochemical sensor based on adaptive nanowires. Trace analysis of a metal (M) analyte in the presence of surface-active compounds (S) using the “active” and “passive” states (with alkanethiol-modified gold/nickel nanowires aligned in the vertical and horizontal positions, respectively). Such adaptive operation leads to “opening” and “closing” of the surface to allow the measurement and protect the transducer between successive measurements. Also shown are the optical images (top view) of the glassy-carbon disk electrode covered with the vertically (left) and horizontally (right) aligned nanowires.

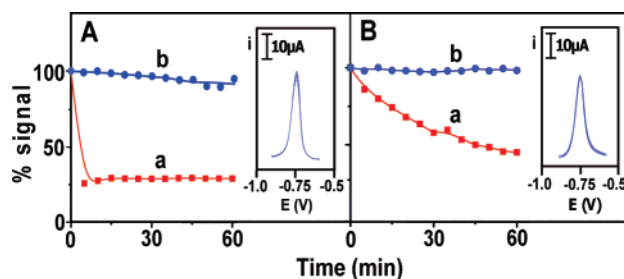


Figure 2. Stability of the cadmium (5 mg L⁻¹) stripping-voltammetric signals in the presence of 10 ppm gelatin (A) and Tween 80 (B) at the bare (a) and nanowires-coated (b) glassy carbon electrodes. Measurements were performed in 5 min intervals, with the sensor “on” for 1 min and “off” for the remaining 4 min. The adaptive nanowires were aligned vertically during the measurements and horizontally between each measurement. Also shown (insets) are corresponding voltammograms (b) over the entire series. Conditions: electrolyte, 0.1 M acetate buffer (pH 4.5); deposition at -1.0 V for 45 s under quiescent condition; scan from -1.0 to -0.5 V. Gold/nickel (50C/20 C) nanowires modified with C18-alkanethiol.

observed in the presence of Tween 80. Such peak diminutions are coupled to 30 mV shifts in the peak potentials along with some peak broadening (not shown). In contrast, the adaptive-nanowire electrode system displays a highly stable response with a negligible change of the peak current over the entire operation. The corresponding voltammograms, shown in the insets, indicate that the peak shape, height, and potential are not affected by the presence of gelatin and Tween 80. Such attractive behavior reflects the protective action imparted by the magnetically oriented nanowires. Apparently, placing the nanowires in the horizontal position between

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successive measurements circumvents surface-fouling effects and leads to a highly stable response.

The optical images of Figure 1 shed useful insights into the protective action of the bi-segment adaptive nanowires. The top view of the “vertical” nanowires (left) indicates that the “islandlike” bundle structure of the vertically oriented nanowires exposes a major portion of the surface of the glassy-carbon disk (dark region). Such magnetically oriented aggregated nanostructures have been observed earlier and reflect the attractive forces between nanowires.¹¹ This vertical (active) state thus allows facile deposition and stripping of metals on the electrode surface and hence convenient electrochemical measurements. In contrast, the surface is fully covered by these nanowire bundles when the adaptive nanowires are reoriented in the “horizontal” position (right). Such a “passive” state blocks completely the surfactant access to the surface to offer the necessary protection between repetitive measurements.

Different variables influencing the resistance to surface fouling, including the chain length of the alkanethiol layer and the relative length of the gold and nickel segments, were optimized. Varying the chain length of the alkanethiol film has a profound effect upon the access of the surface-active macromolecules to the surface and upon the resulting protective action. This is illustrated in Supporting Information Figure 1 for repetitive measurements of cadmium in the presence of gelatin, using a homologous series of alkanethiols with chain lengths ranging from C8 (b) to C18 (d), along with the bare gold nanowires (a). The response of the uncoated nanowires decreases rapidly to 53% of its initial value within a 5 min exposure to gelatin, and diminishes more slowly to 48% within 1 h. Smaller peak diminutions to 70 and 55% after 1 h are observed at C8 and C12 modified nanowires, respectively. The highest protective action is obtained using the C18-modified gold/nickel nanowires with only 4% decrease in the response following 1 h. The high resistance to surface fouling observed with the longest chain length reflects the higher surface density and packing of the C18 monolayer.¹²

The protective action of adaptive nanowires is also strongly influenced by the relative lengths of the gold and nickel segments. Figure 2 in Supporting Information examines the influence of the gold/nickel segment-length ratio upon the resistance to fouling (using a C18 coating). Nanowires with a gold/nickel length ratio of 5 offer effective protection against fouling in the presence of gelatin, with less than 4% signal diminutions following a 60 min exposure (c). The protection efficiency decreases upon decreasing the length ratio to 3 (b) and 1 (a), with 29 and 63% current diminutions, respectively, after a 60 min exposure to gelatin.

The optimal conditions lead to an attractive sensor behavior, with an effective protection against passivation over extended periods of time. Figure 3A displays repetitive stripping voltammograms for cadmium (in the presence of bovine serum albumin (BSA)) obtained over a 3 h period at 30 min intervals at the bare (inset) and the nanowires-coated electrodes (a–g). A significant (~80%) decrease of the response of the bare electrode is observed within the initial 30 min of operation in the presence of BSA. In contrast, highly stable cadmium signals are observed at the nanowire-coated electrode over this prolonged operation. The results confirm that the horizontally aligned nanowires provide an effective barrier to surface-active substances and enable the initial response characteristics to be maintained over long periods in the presence of such surfactants. The significantly (~4-fold) smaller response observed using the horizontal alignment versus the vertical position (not shown) indicates that this conformation is accessible to the small target analyte.

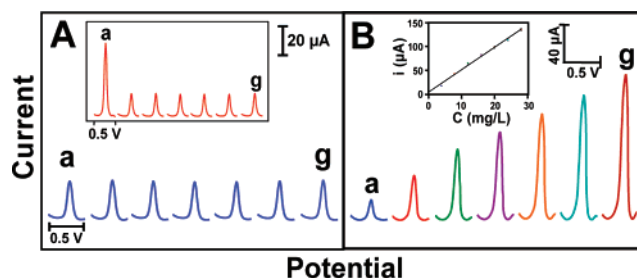


Figure 3. (A) Extended operation in the presence of bovine serum albumin (BSA). Shown are the stripping voltammograms of 5 mg L⁻¹ cadmium in the presence of 10 ppm BSA at the bare (inset) and nanowires-coated electrode. Consecutive measurements were performed every 30 min (a–g). (B) Stripping voltammograms for increasing levels of cadmium in 4 mg L⁻¹ steps (a–g) obtained using the vertical position. Also shown (inset) is the corresponding calibration plot. Other conditions are as described in Figure 2.

The adaptive nanowire-based electrochemical stripping detection results in a well-defined concentration dependence. Figure 3B displays stripping voltammograms obtained for increasing cadmium concentration in 4 mg L⁻¹ steps (a–g). Well-defined peaks, proportional to the metal concentration, are observed, leading to a highly linear calibration plot (inset).

In conclusion, we have demonstrated the use of adaptive nanowires for switching on-demand the operation of electrochemical sensors between active and passive modes. Setting the sensor in the passive mode, between successive measurements, dramatically extends the lifetime of the device in the presence of surface-active macromolecules. While the concept has been illustrated in connection to prolonged monitoring of toxic metals it can be readily extended to a wide range of sensing applications and scenarios. Such on-demand protection capability should lead to the next-generation of “smart” analytical devices which recognize changes in the surrounding environment and then auto-reconfigure themselves on the basis of the results.

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Supporting Information Available: Experimental details and additional data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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