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Magneto-switchable electrogenerated biochemiluminescence

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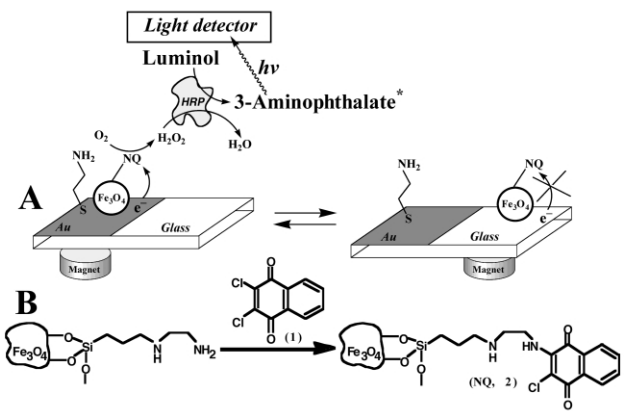
Received (in Cambridge, UK) 25th October 2001, Accepted 3rd December 2001
First published as an Advance Article on the web 20th December 2001

Magnetic-field-stimulated 'ON' and 'OFF' biochemiluminescence is accomplished by electrocatalyzed reduction of naphthoquinone-functionalized magnetic particles in the presence of a biocatalytic peroxidase/luminol system.

Signal-triggered chemical functionalities in molecular, macromolecular and particulate systems are of substantial interest for the development of information storage and processing systems,[1] nanoscale and microscale machines[2] or actuators,[3] signal-triggered transport systems[4,5] or reversible sensor devices.[6] Chemical stimuli such as pH-changes,[7] the addition of ions[8] or the binding of π-acceptor units,[9] were applied to switch the optical properties, *e.g.* fluorescence of molecular or polymer substrates. Photonic switching of chemical functions was achieved in the presence of photoisomerizable components,[10] and photoisomerizable redox-active molecular assemblies on surfaces were applied as nanoengineered systems for the electronic transduction of recorded photonic information.[11] Similarly, the coupling of photoisomerizable units to redox-proteins assembled on electrodes enabled the 'ON' and 'OFF' bioelectrocatalytic activation of redox-enzymes by light.[12] Electrochemical switching of chemical or physical properties of molecular, macromolecular or biomolecular systems has also been reported.[13,14] Recently, we reported on the magnetic switching of redox-processes and specifically bioelectrocatalytic transformations.[15] Here we report on the magneto-switchable generation of light by a magneto-controlled electrogenerated chemiluminescence process.

Scheme 1(A) outlines the system for the magneto-switchable electrogenerated chemiluminescence. Magnetic particles (Fe_3O_4, saturation magnetization *ca.* 65 emu g^{-1}, *ca.* 1 μm average diameter) were prepared according to the published procedure[16] without including the surfactant in the reaction medium. The magnetic particles were silanized with [3-(2-aminoethyl)aminopropyl]trimethoxysilane. 2-Amino-3-chloro-1,4-naphthoquinone-functionalized magnetic particles were prepared by the reaction of 2,3-dichloro-1,4-naphthoquinone (**1**) with aminopropylsiloxane-functionalized[17] magnetite particles, Scheme 1(B). The aminonaphthoquinone (**2**)-modified magnetic particles, 10 mg, were introduced into an electrochemical cell that included one horizontally positioned working Au-electrode (*ca.* 2 cm^2) and a non-conductive glass plate (*ca.* 2 cm^2). A 5-mm diameter magnet (NdFeB/Zn-coated magnet with a remanent magnetization of 10.8 kG) was used to move the aminonaphthoquinone-functionalized magnetic particles between the Au-electrode and the glass plate. Assuming a homogeneous deposition of the magnetic particles on the electrode, the amount of the magnetic particles used in our study translates to a surface coverage of *ca.* 20 layers of particles on the conductive support. Electrochemical reduction (EG&G model 6310 potentiostat) of the quinone under oxygen yields H_2O_2.[18] The electrogenerated H_2O_2 reacts with luminol in the presence of horseradish peroxidase (HRP) to yield 3-aminophthalate and light, (λ_{em} = 425 nm).[19] Lateral translocation of the magnetic particles to a non-conductive domain, by the external movement of the magnet, blocks the electrocatalytic generation of H_2O_2 and the subsequent light emission. Recollection of the particles on the electrode by moving the external magnet reactivates the electrogenerated light emission. A detector (Laserstar, Ophir), linked to an oscilloscope (Tektronix TDS 220), placed on the top of the electrochemical cell, detects the time-dependent light-emission from the system.

The base Au-electrode was modified with cystamine in order to increase the overpotential for the direct electrochemical reduction of O_2.[20] Fig. 1(a) shows the cyclic voltammogram of the cystamine-modified electrode, under argon, when the aminonaphthoquinone-modified magnetic particles are restricted to the non-conductive domain. Fig. 1(b) shows the electrical response of the quinone-modified magnetic particles attracted to the Au-surface by the appropriate positioning of the external magnet. It is assumed that the quinone units of all particles are electrochemically contacted with the electrode by electron hopping through the redox units. By the coulometric



Scheme 1 (A) Magneto-triggered biochemiluminescence and (B) functionalization of silanized magnetic particles with naphthoquinone units.

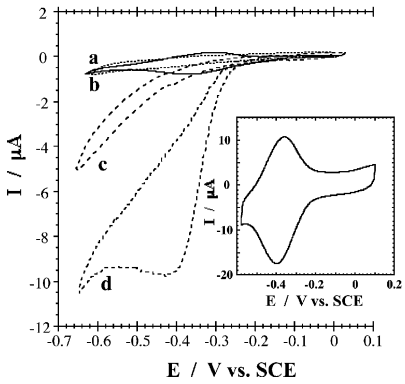


Fig. 1 Cyclic voltammograms of: (a) the cystamine-modified Au-electrode under Ar (dashed line); (b) the magnetically-attracted naphthoquinone-modified particles (10 mg) under Ar (solid line); (c) the cystamine-modified Au-electrode under air; (d) the magnetically-attracted naphthoquinone-modified particles (10 mg) under air. All experiments recorded in 0.1 M phosphate buffer, pH 7.0, potential scan rate, 10 mV s^{-1}. Inset: Cyclic voltammogram of the system described in (b), potential scan rate, 100 mV s^{-1}.

DOI: 10.1039/b109782m

assay of the quinone redox-wave (see Fig. 1, inset, obtained at high scan rate), the average loading is estimated to be *ca.* 1000–2000 quinone units per magnetic particle. Fig. 1(c) and (d), show the electrical responses of the electrode under oxygen when the quinone-modified magnetic particles are restricted to the non-conductive domain and to the cystamine-modified Au-electrode, respectively, by means of the external magnet. Clearly, magnetic attraction of the quinone-functionalized particles stimulates the electrocatalytic reduction of oxygen. In the potential region $E > -0.4$ V (*vs.* SCE), the cystamine-modified electrode lacking the particles, is inactive towards O_2-reduction, whereas the naphthoquinone-functionalized magnetic particles catalyze the electrochemical reduction of O_2 in the potential region $E < -0.36$ V. Constant-potential electrolysis of O_2 at $E = -0.4$ V (*vs.* SCE) in the presence of the magnetically-attracted naphthoquinone-functionalized magnetic particles yields H_2O_2 that was identified coulometrically[21] (current yield 87%).

Fig. 2 depicts the magneto-switchable electrogenerated chemiluminescence. Chronoamperometric potential steps from 0.0 to −0.4 V (*vs.* SCE) are applied on the electrode, Fig. 2(A). In steps 1 and 2 the quinone-functionalized magnetic particles are attracted by the external magnet to the Au-electrode. Steps 3 and 4 are applied on the electrode when the magnetic particles are translocated by the external magnet to the non-conductive domain. The potential step 5 is applied on the electrode when the functional magnetic particles are re-collected on the electrode surface by means of the external magnet. The potential steps presented in cycles 1 and 2, where the quinone-functionalized magnetic particles rest on the electrode, reveal an amperometric response as a result of the electrocatalytic reduction of oxygen. Concomitantly, light is generated in the system, as shown in Fig. 2(B), with the light pulses 1′ and 2′. Translocation of the functionalized-particles to the non-conductive domain of the cell results in, upon the application of the potential steps 3 and 4 to the electrode, very low amperometric responses that may be attributed to the double-layer charging of the electrode, and eventually minute quantities of residual magnetic particles. The light-emission from the system upon the application of these potential steps is almost blocked, Fig. 1(B), cycles 3′ and 4′. Further magnetic shift of the functionalized magnetite particles to the electrode switches on the current response and the light emission upon the application of the potential step on the electrode, Fig. 2, cycles 5 and 5′, respectively.

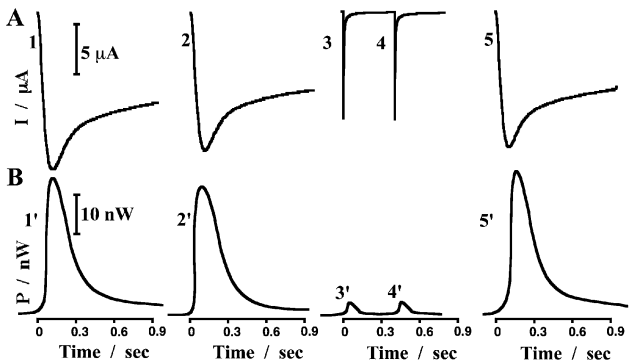


Fig. 2 Magneto-switchable electrocatalytic generation of biochemiluminescence in a system consisting of the naphthoquinone-functionalized magnetic particles (10 mg), luminol (1×10^{-6} M) and HRP (1 mg mL^{-1}). (A) Chronoamperometric transients upon the application of potential steps from 0.0 to −0.4 V (*vs.* SCE) on the cystamine-modified Au-electrode: current transients 1, 2 and 5 — the functionalized particles are positioned on the Au-electrode by the external magnet. Current transients 3 and 4 — the functionalized particles are translocated to the non-conductive glass support by the external magnet. (B) Light emitted from the system upon the application of the respective chronoamperometric transients. All measurements were performed in 0.1 M phosphate buffer, pH 7.0, system equilibrated with air.

In conclusion, we demonstrate the assembly of a system that leads to the reversible and cyclic magneto-switchable electrochemical generation of light. The system reveals functions of a logic 'AND' gated element. That is, light emission occurs only if the quinone-functionalized particles are associated with the electrode support, and provided that the appropriate potential step is applied on the electrode for the electrocatalytic generation of H_2O_2.

This research is supported by The Israel Science Foundation administrated by the Israel Academy of Sciences and Humanities.

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