J|A|C|S
COMMUNICATIONS

Published on Web 05/02/2007

Photoswitchable Electrocatalysis and Catalyzed Chemiluminescence Using Photoisomerizable Monolayer-Functionalized Surfaces and Pt Nanoparticles

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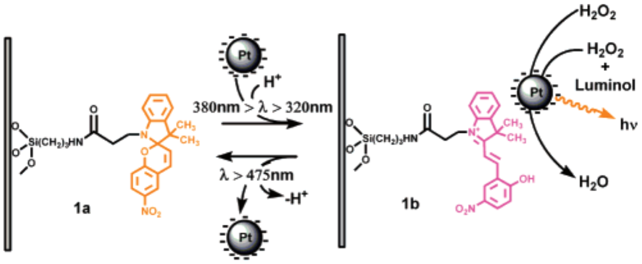
Photoisomerizable monolayers associated with electrodes attract scientific interest as active materials for information storage and processing.[1] The photoisomerization of the monolayers between two distinct states provides chemical unit mimics that act as the "0" and "1" states in computers. The electronic readout of one of the photoisomer states (or both) provides then "write−read−erase" systems. The photoisomer states of different light-induced isomerizable monolayers were transduced by the electrochemical activity of one of the photoisomer states[2,3] or by following the difference in the tunneling currents between the two photoisomer structures.[4] Alternatively, the selective attraction (or repulsion) of redox-active molecules[5] or biomolecules[6] to (or from) charged photoisomers linked to the electrode was used as a means to readout the photoisomer states associated with the electrode. Also, photoswitchable bioelectrocatalytic processes were developed by the selective binding of biocatalysts to charged photoisomer monolayers associated with electrodes,[7] and the reactions were suggested as a means to amplify the readout signals of the photoisomer states. Here we wish to report on the photoswitchable electrocatalysis and photoswitchable catalytic generation of chemiluminescence using Pt nanoparticles (NPs) as catalysts. As far as we are aware, such systems are unprecedented.

Pt NPs were recently employed as labels for the amplified analysis of DNA or aptamer−protein interactions using the Pt-electrocatalyzed reduction of H_2O_2 or the NP-catalyzed generation of chemiluminescence as readout signals.[8] The Pt NPs were prepared by the reduction of H_2PtCl_6 with citrate. The diameter of the resulting negatively charged NPs was determined by SEM to be in the range of 20−30 nm. The system for the photoswitchable electrocatalyzed reduction of H_2O_2 is schematically depicted in Scheme 1.

The nitrospiropyran derivative (**1a**) was assembled on an indium tin oxide (ITO) electrode. Propionic acid-functionalyzed nitrospiropyran was coupled to an aminopropylsiloxane-modified ITO surface using 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) as coupling reagent. The surface coverage of (**1a**) was determined[9] electrochemically by following the irreversible $4e^-/4H^+$ reduction of the nitro group to the respective hydroxylamine group, and it corresponded to 2.9×10^{-11} mole•cm^{-2}.(Note that the electrodes employed for the determination of the surface coverage were discarded and not used for the photoswitching experiments since the electrochemically reduced monolayer lacks photoisomerizable functions.)

Scheme 1. Photoswitchable Electrocatalyzed Reduction of H_2O_2 and the Catalytic Generation of Chemiluminescence at Surfaces Modified with a Photoisomerizable Monolayer in the Presence of Pt NPs



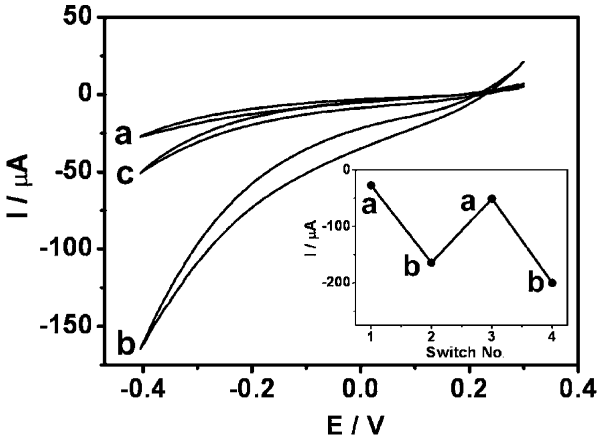


Figure 1. Cyclic voltammograms corresponding to (a) the SP monolayer-modified ITO electrode treated with Pt NP in the presence of H_2O_2, (b) the MRH^+ monolayer-functionalized electrode in the presence of Pt NPs and H_2O_2, and (c) the back photoisomerization of the monolayer to the SP state and treatment of the system with Pt NPs, and H_2O_2. Data were recorded from solutions of 10 mM phosphate buffer (pH = 7.3) using H_2O_2 (71 mM) and Pt NPs (6 nM); scan-rate = 100 mV•s^{-1}. The inset shows photoswitchable amperometric responses of the photoisomerizable electrode treated with Pt NPs/H_2O_2 in the presence of (a) the SP state and (b) the MRH^+ state.

The nitrospiropyran monolayer (SP) lacks affinity for the negatively charged Pt NPs and hence is catalytically inactive toward the reduction of H_2O_2. The photoisomerization, $380 > \lambda > 320$ nm, of the monolayer to the nitro merocyanine photoisomer is accompanied by the protonation of the zwitterion and the formation of the protonated nitro merocyanine monolayer, MRH^+, (**1b**) (pK_a of the nitro merocyanine is ca. 7.0). The resulting positively charged monolayer attracts the Pt NPs to the surface, leading to the NP-modified electrode that catalyzes the reduction of H_2O_2. Back photoisomerization of the MRH^+-monolayer to the SP-monolayer state by visible light irradiation, $\lambda > 475$ nm, leads to the detachment of the Pt NPs and to the formation of a catalytically inactive electrode. Thus, by the cyclic photoisomerization of the monolayer between the SP- and MRH^+-monolayer states, the electrode is reversibly switched between inactive (OFF) and active (ON) electrocatalytic states, respectively. Figure 1, curve a shows the cyclic voltammogram corresponding to the SP-modified electrode treated with the Pt NPs in the presence of H_2O_2. No electrocatalytic current is observed, implying that the electrode is in the inactive-OFF state. Photoisomerization of the electrode to

10.1021/ja0707052 CCC: $37.00 © 2007 American Chemical Society

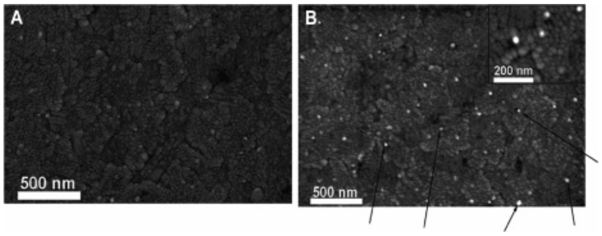


Figure 2. SEM images of (A) the SP-modified ITO surface treated with Pt NPs and (B) the MRH$^+$-modified ITO surface treated with Pt NPs (arrows indicate Pt NPs).

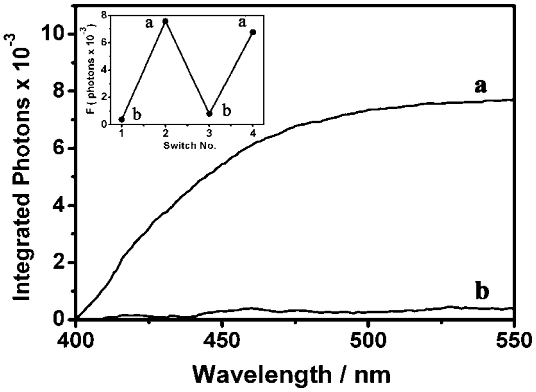


Figure 3. Integrated light intensities generated by (a) the MRH$^+$-functionalized glass surface and (b) the SP-functionalized glass surface, upon treatment with Pt NPs, (6 nM) and reaction with luminol (6 mM) and H_2O_2 (71 mM) in 10 mM phosphate buffer, pH = 8.3. The inset shows the cyclic photoswitchable chemiluminescence generated by (a) the SP-modified surface and (b) the MRH$^+$-modified surface.

the MRH$^+$ monolayer and the treatment of the electrode with the Pt NPs yield, in the presence of H_2O_2, the cyclic voltammogram shown in Figure 1, curve b. The electrocatalytic cathodic current indicates that the Pt-catalyzed reduction of H_2O_2 proceeds. Further photoisomerization of the MRH$^+$ monolayer to the SP state results in the removal of the Pt NPs from the electrode and the formation of a catalytic inactive electrode, Figure 1, curve c. By the cyclic photoisomerization of the monolayer between the SP and MRH$^+$ states, the electrode was reversibly switched between OFF and ON states, respectively (Figure 1, inset). We were able to photoswitch the electrocatalytic functions of the electrode for 10 cycles with no significant degradation of the modified electrode.

The facilitated charge transport associated with the Pt NPs-functionalized electrode that mediates the catalyzed reduction of H_2O_2 was further supported by impedance measurements. While the electron-transfer resistance of the SP-functionalized electrode in the presence of the Pt NPs/ H_2O_2 corresponded to 2.4 ± 0.2 kΩ, the value of the interfacial electron-transfer resistance of the MRH$^+$-modified electrode in the presence of the Pt NPs/ H_2O_2 corresponded to 1.7 ± 0.2 kΩ,(see S1 in Supporting Information).

Further support for the selective association of the Pt NPs to the MRH$^+$ electrode was obtained by SEM experiments. Figure 2, panels A and B show the SEM images of the SP- and MRH$^+$-modified electrodes after treatment with the negatively charged Pt NPs, respectively. While no Pt NPs were bound to the SP-monolayer modified ITO surface, the MRH$^+$ monolayer-functionalized ITO surface is covered with tightly bound Pt NPs.

The photoisomerizable monolayer associated with the electrode, in conjunction with the Pt NPs as catalysts and luminol/H_2O_2 as substrates, was also employed for the catalyzed generation of chemiluminescence, Scheme 1.

Figure 3, curve a shows the integrated light intensity generated by the MRH$^+$-monolayer-modified surface that was treated with the Pt NPs in the presence of H_2O_2/luminol. Photoisomerization of the monolayer to the SP state resulted in the removal of the Pt, and only a residual light intensity is observed upon treating the electrode with H_2O_2/luminol (Figure 3, curve b). By the cyclic photoisomerization of the monolayer between the MRH$^+$- and SP-monolayer states, and interacting the surface with Pt NPs and H_2O_2/luminol, the chemiluminescence generated by the system was switched between ON and OFF states, respectively.

To conclude, the present study has demonstrated the use of a surface-confined photoisomerizable monolayer that was coupled to negatively charged Pt NPs, for the photoswitchable electrocatalysis and the photostimulated ON−OFF generation of chemiluminescence. The photoswitchable functions of the respective surfaces originated from the selective electrostatic association of the negatively charged NPs to the positively charged MRH$^+$ monolayer-functionalized electrode.

Acknowledgment. This research is supported by the MOLDYNLOGIC EC Project.

Supporting Information Available: The cyclic activity and electron-transfer resistances of the photoswitchable electrocatalytic system, and control experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA0707052