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Light-Driven OR and XOR Programmable Chemical Logic Gates

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Currently used logic devices are based on monolithic semiconductor structures. Further development (i.e., miniaturization) of these devices is limited by technological and physical factors.[1] Application of chemical structures for information processing seems to be a solution that can, at least temporarily, sustain the development of information technologies.[2−7] Moreover, light seems to be the most efficient medium for communication between chemical logic systems.[8,9]

Computers are based on binary logic. All the information is encoded in series of zeros and ones. Logic gates are basic elements processing information; they function as switches whose output (0 or 1) depends on input conditions. There is a multitude of chemical systems capable of performing similar type of operations. Most of these systems are based on solutions containing switching molecules. Information to be processed is supplied as variation of concentration of various chemicals, while the output is read as fluorescence or absorbance of the solution. This approach makes the integration of chemical logic devices with currently used electronic equipment extremely difficult, the same concerns more advanced processing involving various logic gates connected into more complex systems. Moreover, some logic gates, such as XOR, are very difficult to implement in chemical systems. In most cases, the XOR operation is based on annihilation of two chemical inputs, such as acid and base or metal ion and chelating agent.[5,10] This approach does not allow more advanced information processing. This communication describes the first example of a chemical optoelectronic XOR gate operated exclusively by optical inputs and electric output. Furthermore, the system can be programmed to various modes of operation by simple control of the photoelectrode potential.

Surface-modified nanocrystalline semiconductors also serve as very powerful and diverse switching devices.[11] Several logic systems, including AND, OR, and INHIBIT gates, based on photoelectrodes made of cyanoferrate modified TiO_2, use light and potential signals as input data and yield information encoded in current pulses.[11] These features make this system much more suited to cooperate with existing silicon-based devices.

Titanium dioxide is easily modified with $[Fe^{II}(CN)_5L]^{n-}$ complexes ($L = CN^-$, H_2O, NH_3, thiodiethanol, thiodipropanol). These complexes bind the surface of nanocrystals via formation of cyanobridged species, such as $L(CN)_4Fe^{II}{-}C{\equiv}N{-}Ti^{IV}$.[11−14] These materials exhibit unique photoelectrochemical properties in air-equilibrated electrolyte solutions. Upon electrochemical oxidation of the surface complex, the electrode generates anodic photocurrent like neat titanium dioxide. Partial reduction of the surface complex results in appearance of an MMCT ($Fe^{II} \rightarrow Ti^{IV}$) transition.[11−14] Excitation within this band results in generation of cathodic photocurrent due to an electron transfer from the excited surface complex to an electron acceptor in solution (Figure 1).[11] At the same time, excitation within the semiconductor absorption band generates anodic photocurrent. Complete reduction of the surface complex results in formation of an inversion layer within the semiconductor particles, and generation of cathodic photocurrent is observed within the whole absorption spectrum of the material (Figure 1).

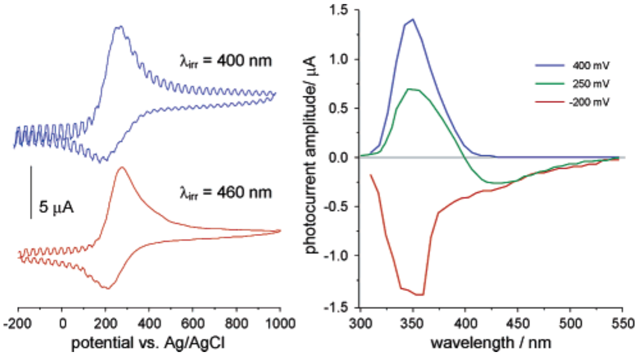

Figure 1. Cyclic voltammograms of $[Fe(CN)_6]^{4-}$ modified titanium dioxide photoelectrode upon pulsed irradiation with LEDs (left) and photocurrent action spectra of this electrode recorded under potentiostatic conditions (right).

Photocurrent generated at described photoelectrodes can be switched from anodic to cathodic (or opposite) by applying various potentials (Figure 1, left) or various photon energies (Figure 1, right, curve recorded at 250 mV). Due to these two main factors affecting the net photocurrent effect, we have proposed to name this phenomenon as *P*hoto*E*lectrochemical *P*hotocurrent *S*witching (*PEPS*) effect.[11]

Competition between cathodic and anodic photocurrents can be applied to mimic the XOR logic gate. This gate yields high output value (logical 1) when input values are different (i.e., 0 and 1). Two identical input values (0, 0 or 1, 1) yield zero as an output.

In construction of an optical logic system based on nanocrystalline TiO_2 photoelectrodes modified with cyanoferrates, electroluminescent diodes were used as light sources. Diodes were powered by a pulse generator allowing for quasi-monochromatic (400 or 460 nm) or quasi-bichromatic (400 and 460 nm) pulsed irradiation (Figure 2).

To analyze the system in term of Boolean logic, it is necessary to assign logic values to input and output signals. For the sake of simplicity, logical 0 and 1 are assigned to off and on states of the LEDs, respectively. Two different wavelengths correspond to two different inputs of the logic gate. In the same way, one can assign logic 0 to the state when photocurrent is not generated and logic 1 to any nonzero photocurrent intensity irrespectively on its polarization (cathodic or anodic).

At potentials ensuring complete oxidation of the surface species (e.g., +400 mV vs Ag/AgCl), pulsed irradiation with violet diode (λ_{max} = 400 nm) results in anodic photocurrent pulses, while irradiation with blue LED (λ_{max} = 460 nm) does not generate any photocurrent. Simultaneous irradiation with two LEDs yields the same effect as the violet diode alone (Figure 2, Table 1, output 1). Electrochemical reduction of the surface species is achieved at lower potentials. Excitation of this material with violet and blue diodes

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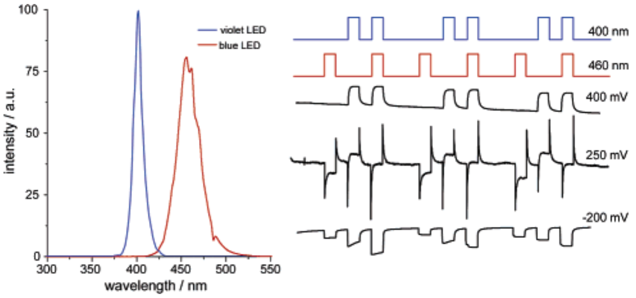

Figure 2. Emission spectra of violet and blue LEDs used for illumination (left) and photocurrent profiles recorded during pulsed irradiation of $[Fe(CN)_6]^{4-}$ modified titanium dioxide photoelectrodes (right). Power density at the electrode surface (measured with Ophir Nova II radiant power meter equipped with PD300-UV head) is 1.4 and 2.0 mW cm^{-2} for 400 and 460 nm diode, respectively. Diodes operate at input power of 35 and 38 mW, respectively. The electrode surface is ca. 1 cm^2.

Table 1. Truth Table for Logic Gates Based on $[Fe(CN)_6]^{4-}$ Modified Titanium Dioxide Photoelectrodes. Outputs 1, 2, and 3 Refer to Photoelectrochemical Responses at Given Potentials

input 1 400 nm	input 2 460 nm	output 1 400 mV	output 2 250 mV	output 3 –200 mV
0	0	0	0	0
0	1	0	1	1
1	0	1	1	1
1	1	1	0	1
		YES	XOR	OR

leads to generation of cathodic photocurrent. Simultaneous irradiation by both diodes results in higher intensity of photocurrent. Such behavior of the photoelectrode at −200 mV vs Ag/AgCl corresponds to the OR logic gate (Figure 2, Table 1, output 3).

Much more interesting photocurrent profiles were recorded upon partial oxidation of the surface complex. Irradiation with 400 nm light results in generation of anodic photocurrent, which is consistent with excitation of the inner part of semiconductor particles. Irradiation with 460 nm light results in generation of cathodic photocurrent. Simultaneous irradiation with two diodes gives zero net current as anodic and cathodic photocurrents compensate effectively (Figure 2, Table 1, output 2). This behavior analyzed in terms of Boolean logic corresponds to the XOR gate. The photocurrent compensation, however, requires such adjustment of light intensity of both sources that absolute values of anodic and cathodic photocurrents are equal. This can be easily achieved here by adjustment of diode supply current. Due to specific photocurrent development kinetics observed in the case of TiO_2 photoelectrodes, it is not possible to observe complete compensation of photocurrents. Therefore, residual spikes at the beginning and end of every illumination period appear. The complete compensation, however, is observed for photostationary conditions.

The chemical system described above is a simple functional model of logic gates. Information is supplied to the system by means of light pulses, and processed information is retrieved in the form of current pulses. This behavior is quite unique for chemical logic systems and allows facile communication between various electronic silicon-based devices and chemical logic system.

The logic device based on semiconducting photoelectrodes shows another important feature. It should be noted that the logic analysis of this systems can be much more complex if photoelectrode potential is considered as the third input channel. In this context, the logic system described here is a chemical model of a reconfigurable logic device, the function of which can be programmed by the user.[15,16] Changes in applied potential can switch the logic behavior of the photoelectrode between three different regimes: (i) transmission of the input 1 signal to the output neglecting input 2 (YES), (ii) computation of the XOR function of two input values, and (iii) computation of the OR function of two input values (Figure 3).

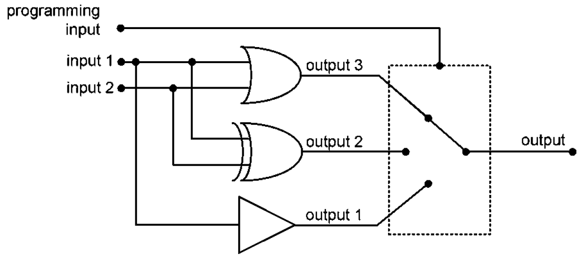

Figure 3. Electronic equivalent circuit for reconfigurable logic system based on modified titanium dioxide electrode. Output 1 follows the input 1 signal, output 2 computes the XOR function of input data, while output 3 corresponds to the logic sum (OR) of input data. Programming input and three-position switch represent programming of the device through the photoelectrode potential.

Reconfigurability (variation of logic device function upon programming or stimulation) of the chemical logic device is a unique feature. Numerous chemical systems are capable of mimicking logic functions, but the response of these systems is intrinsically associated with chemical structure of the switch. Application of a nanocrystalline semiconductor modified with electrochemically and photochemically active compounds opens a possibility for further development of chemical logic systems.

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